DR/820
COLORIMETER
PROCEDURES MANUAL

te/dk 03/13 6ed

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INTRODUCTION

This manual is divided into five sections:

Section 1 Chemical Analysis Information

This section applies to all the procedures. It provides background information and reference/review material for the technician or chemist. Commonly used techniques are explained in detail.

Section 2 Sample Pretreatment

This section provides a brief overview of sample pretreatment and two USEPA digestions. A brief discussion of the Hach Digesdahl Digestion Apparatus and the Hach Distillation Apparatus is included.

Section 3 Waste Management and Safety

Section 3 includes information on waste management, regulations, waste disposal and resources on waste management. The Safety portion covers reading an MSDS and general safety guidelines.

Section 4 Procedures

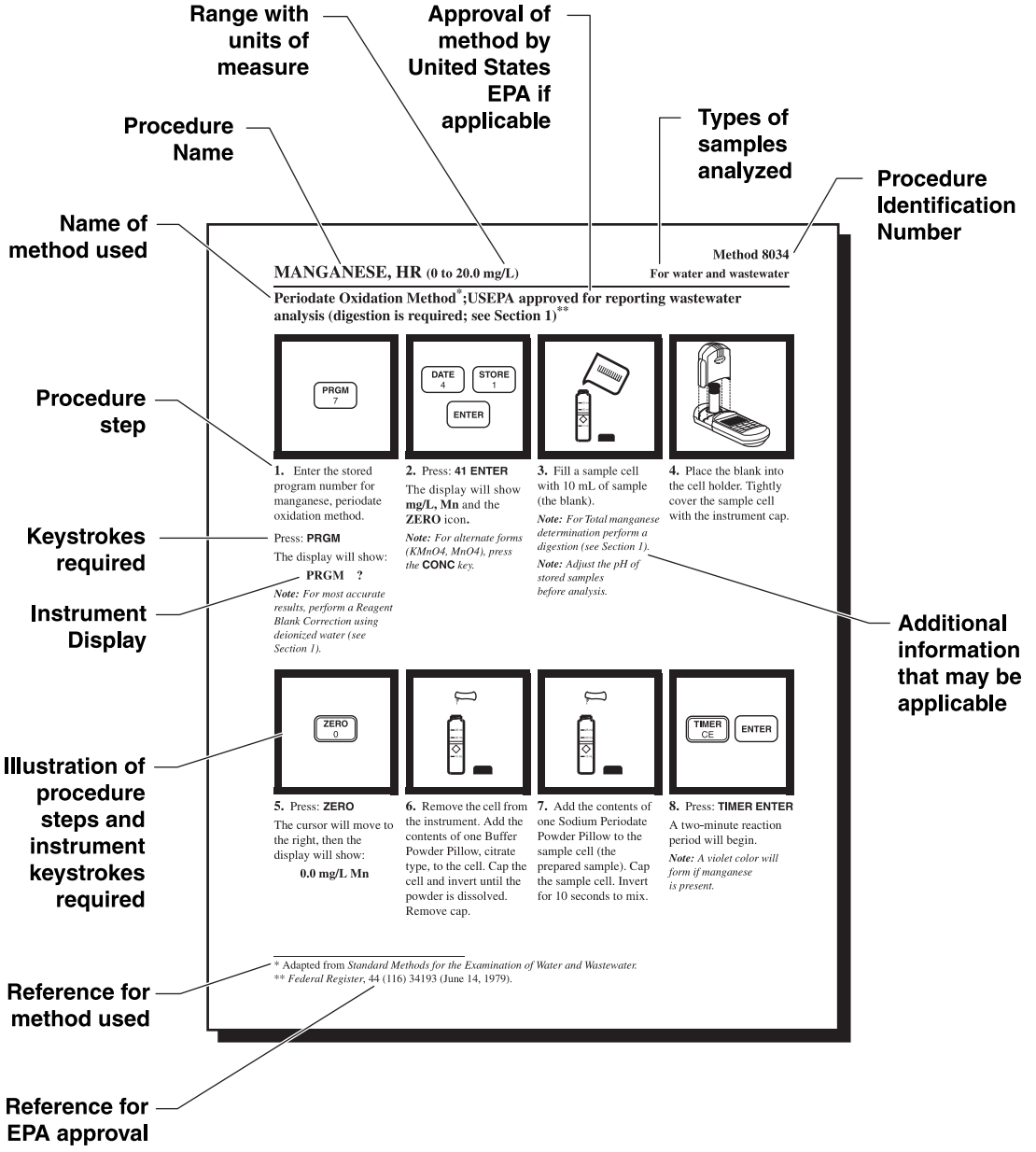
Section 4 contains step-by-step illustrated instructions for measuring parameters. The steps also include helpful notes. Each procedure contains information on sample collection, storage and preservation, accuracy checks, possible interferences, summary of method and a list of the reagents and apparatus necessary to run the test.

Section 5 Ordering Information

This section provides information needed for ordering, shipping, return of items and Hach trademarks.

Before attempting the analysis procedures the analyst should read the instrument manual to learn about the colorimeter's features and operation.

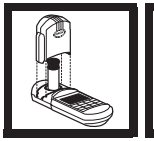
Sample Procedure Explained



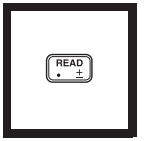
Specific sampling and storage information for this test

Confirm accuracy with these steps (in addition, may also be used to troubleshoot a test, improve technique, check reagents and to assure cleanliness of glassware)

MANGANESE, HR, continued



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L manganese will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in acid-washed plastic bottles. Manganese may be lost by adsorption to glass container walls. Adjust the pH to less than 2 with nitric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature. Adjust the pH to 4 to 5 with 5.0 N sodium hydroxide before analysis. Do not exceed pH 5, as manganese may be lost as a precipitate. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section 1* for more information. If only dissolved Mn is to be determined, filter before acid addition.

Accuracy Check

Standard Additions Method

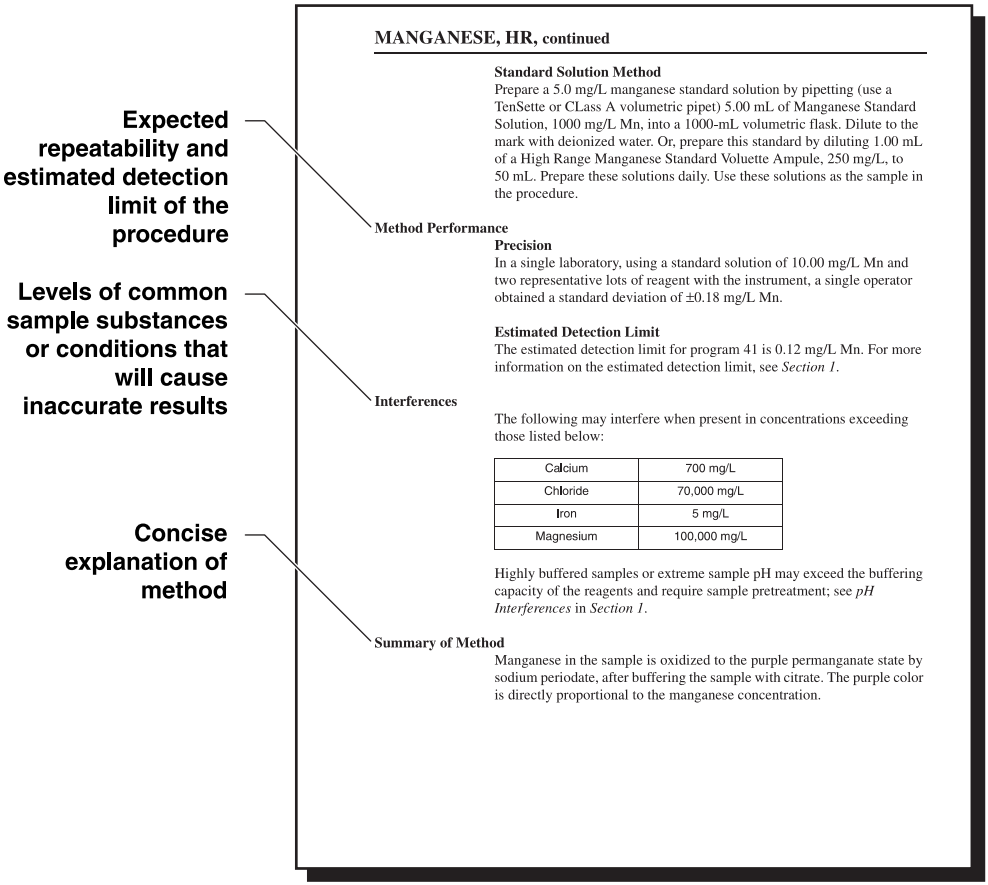
a) Snap the neck off a Manganese Voluette Ampule Standard Solution, 250 mg/L Mn.

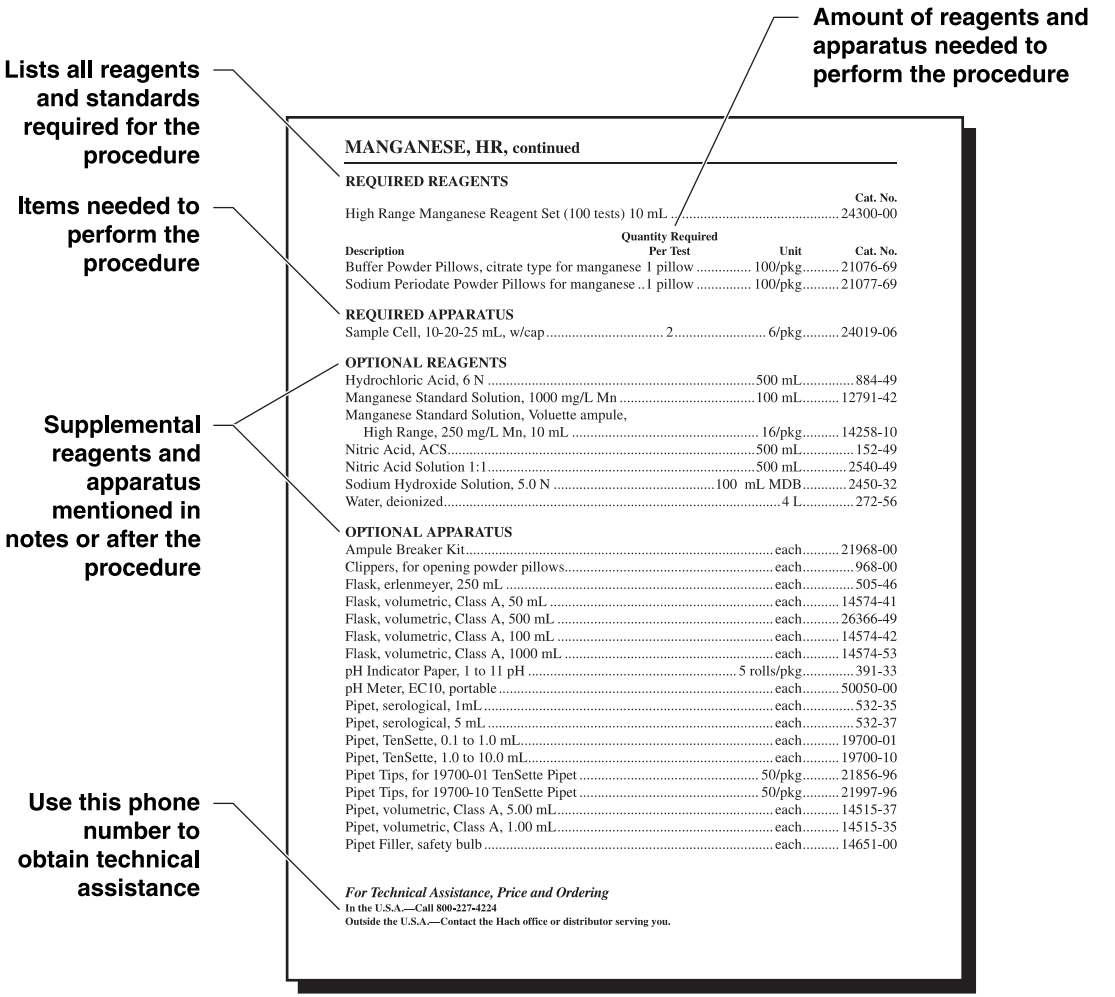
b) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard, respectively, to the three 25-mL water samples. Swirl to mix.

c) Transfer only 10 mL of each solution to the 10-mL sample cells.

d) Analyze each standard addition sample as described in the procedure. The manganese concentration should increase 1.0 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* in *Section 1* for troubleshooting information.


Expected repeatability and estimated detection limit of the procedure
Levels of common sample substances or conditions that will cause inaccurate results
Concise explanation of method
MANGANESE, HR, continued
Standard Solution Method
Prepare a 5.0 mg/L manganese standard solution by pipetting (use a TenSette or CLass A volumetric pipet) 5.00 mL of Manganese Standard Solution, 1000 mg/L Mn, into a 1000-mL volumetric flask. Dilute to the mark with deionized water. Or, prepare this standard by diluting 1.00 mL of a High Range Manganese Standard Voluette Ampule, 250 mg/L, to 50 mL. Prepare these solutions daily. Use these solutions as the sample in the procedure.
Method Performance
Precision
In a single laboratory, using a standard solution of 10.00 mg/L Mn and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.18 mg/L Mn.
Estimated Detection Limit
The estimated detection limit for program 41 is 0.12 mg/L Mn. For more information on the estimated detection limit, see Section 1.
Interferences
The following may interfere when present in concentrations exceeding those listed below:
Calcium 700 mg/L
Chloride 70,000 mg/L
Iron 5 mg/L
Magnesium 100,000 mg/L
Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see pH Interferences in Section 1.
Summary of Method
Manganese in the sample is oxidized to the purple permanganate state by sodium periodate, after buffering the sample with citrate. The purple color is directly proportional to the manganese concentration.



MANGANESE, HR, continued

REQUIRED REAGENTS

			Cat. No.
High Range Manganese Reagent Set (100 tests) 10 mL			24300-00

Description	Quantity Required Per Test	Unit	Cat. No.
Buffer Powder Pillows, citrate type for manganese	1 pillow	100/pkg	21076-69
Sodium Periodate Powder Pillows for manganese	1 pillow	100/pkg	21077-69

REQUIRED APPARATUS

Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Hydrochloric Acid, 6 N	500 mL	884-49
Manganese Standard Solution, 1000 mg/L Mn	100 mL	12791-42
Manganese Standard Solution, Voluette ampule, High Range, 250 mg/L Mn, 10 mL	16/pkg	14258-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution 1:1	500 mL	2540-49
Sodium Hydroxide Solution, 5.0 N	100 mL MDB	2450-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Clippers, for opening powder pillows	each	968-00
Flask, erlenmeyer, 250 mL	each	505-46
Flask, volumetric, Class A, 50 mL	each	14574-41
Flask, volumetric, Class A, 500 mL	each	26366-49
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, 1mL	each	532-35
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet, TenSette, 1.0 to 10.0 mL	each	19700-10
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-10 TenSette Pipet	50/pkg	21997-96
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet Filler, safety bulb	each	14651-00

For Technical Assistance, Price and Ordering
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

SECTION 1 CHEMICAL ANALYSIS INFORMATION

Abbreviations

The following abbreviations are used throughout the text of the procedure section:

Abbrev-iation	Definition	Abbrev-iation	Definition
°C	degree(s) Celsius (Centigrade)	MDL	Method detection limit
°F	degree(s) Fahrenheit	MDB	marked dropping bottle
ACS	American Chemical Society reagent grade purity	mg/L	milligrams per liter (ppm)
APHA Standard Methods	*Standard Methods for the Examination of Water and Wastewater.*[1]	µg/L	micrograms per liter (ppb)
AV	AccuVac	mL	(milliliter)-approximately the same as a cubic centimeter (cc) or 1/1000 of a liter. Also known as a “cc”.
conc	concentrated	MR	medium range
CFR	Code of Federal Regulations	NIPDWR	National Interim Primary Drinking Water Regulations
DB	dropping bottle	NPDES	National Pollutant Discharge Elimination System
EDL	Estimated detection limit	PCB	Poly chlorinated biphenyl
FAU	Formazin Attenuation Units. Turbidity unit of measure based on a Formazin stock suspension.	SCDB	self-contained dropping bottle
g	grams	TNT	Test ‘N Tube™
gr/gal	grains per gallon (1 gr/gal = 17.12 mg/L)	TPH	Total petroleum hydrocarbons
HR	high range	TPTZ	(2,4,6-Tri-(2-Pyridyl)-1,3,5-Triazine)
L	Liter. Volume equal to one cubic decimeter (dm^3)	ULR	Ultra low range
LR	low range	USEPA	United States Environmental Protection Agency

[1] Published jointly by the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF). Order from Hach requesting Cat. No. 22708-00 or from the Publication Office of the American Public Health Association. This book is the standard reference work for water analysis. Many procedures contained in this manual are based on *Standard Methods.*

Converting Chemical Species

Species conversion factors for many commonly used substances are pre-programmed into the instrument (see *Table 1*). Conversions are method specific and are viewable after taking the reading by pressing **CONC**.

Table 1 Conversion Factors

To Convert From...	To...	Multiply By...
mg/L Al	mg/L Al_2O_3	1.8895
mg/L Ca-$CaCO_3$	mg/L Ca	0.4004
mg/L $CaCO_3$	mg/L Ca	0.4004
mg/L $CaCO_3$	mg/L Mg	0.2428
µg/L Carbohydrazide	µg/L Hydroquinone	1.92
µg/L Carbohydrazide	µg/L ISA	2.69
µg/L Carbohydrazide	µg/L MEKO	3.15
mg/L Cr^{6+}	mg/L CrO_4^{2-}	2.231
mg/L Cr^{6+}	mg/L Na_2CrO_4	3.115
mg/L Mg-$CaCO_3$	mg/L Mg	0.2428
mg/L Mn	mg/L $KMnO_4$	2.876
mg/L Mn	mg/L MnO_4^-	2.165
mg/L Mo^{6+}	mg/L MoO_4^{2-}	1.667
mg/L Mo^{6+}	mg/L Na_2MoO_4	2.146
mg/L N	mg/L NH_3	1.216
mg/L N	mg/L NO_3^-	4.427
mg/L Na_2CrO_4	mg/L Cr^{6+}	0.321
mg/L Na_2CrO_4	mg/L CrO_4^{2-}	0.72
mg/L NH_2Cl-N	mg/L Cl_2	5.0623
mg/L NH_2Cl-N	mg/L NH_2Cl	3.6750
mg/L NH_3-N	mg/L NH_3	1.216
mg/L NH_3-N	mg/L NH_4^+	1.288
mg/L NO_2^-	mg/L $NaNO_2$	1.5
mg/L NO_2^-	mg/L NO_2^--N	0.3045
mg/L NO_2^--N	mg/L $NaNO_2$	4.926
µg/L NO_2^--N	µg/L $NaNO_2$	4.926
mg/L NO_2^--N	mg/L NO_2^-	3.284
µg/L NO_2^--N	µg/L NO_2^-	3.284
mg/L NO_3^--N	mg/L NO_3^-	4.427
mg/L PO_4^{3-}	mg/L P	0.3261
µg/L PO_4^{3-}	µg/L P	0.3261
mg/L PO_4^{3-}	mg/L P_2O_5	0.7473
µg/L PO_4^{3-}	µg/L P_2O_5	0.7473
mg/L SiO_2	mg/L Si	0.4674
µg/L SiO_2	µg/L Si	0.4674

Hardness Conversion

Table 2 lists the factors for converting one unit of measure for hardness to another unit of measure. For example, to convert mg/L $CaCO_3$ to German parts/100,000 CaO, multiply the value in mg/L x 0.056.

Table 2 Hardness Conversion Factors

Units of Measure	mg/L $CaCO_3$	British gr/gal (Imperial) $CaCO_3$	American gr/gal (US) $CaCO_3$	French parts/ 100,000 $CaCO_3$	German Parts/ 100,000 CaO	meq/L[1]	g/L CaO	lbs./cu ft $CaCO_3$
mg/L $CaCO_3$	1.0	0.07	0.058	0.1	0.056	0.02	$5.6x10^{-4}$	$6.23x10^{-5}$
English gr/gal $CaCO_3$	14.3	1.0	0.83	1.43	0.83	0.286	$8.0x10^{-3}$	$8.9x10^{-4}$
US gr/gal $CaCO_3$	17.1	1.2	1.0	1.72	0.96	0.343	$9.66x10^{-3}$	$1.07x10^{-3}$
Fr. p/ 100,000 $CaCO_3$	10.0	0.7	0.58	1.0	0.56	0.2	$5.6x10^{-3}$	$6.23x10^{-4}$
Ger. p/ 100,000 CaO	17.9	1.25	1.04	1.79	1.0	0.358	$1x10^{-2}$	$1.12x10^{-3}$
meq/L	50.0	3.5	2.9	5.0	2.8	1.0	$2.8x10^{-2}$	$3.11x10^{-2}$
g/L CaO	1790.0	125.0	104.2	179.0	100.0	35.8	1.0	0.112
lbs./cu ft $CaCO_3$	16,100.0	1,123.0	935.0	1,610.0	900.0	321.0	9.0	1.0

[1] 'epm/L, or 'mval/L'
Note: 1 meq/L = 1N/1000

Dissolved Oxygen

Table 3 lists the mg/L dissolved oxygen in water at saturation for various temperatures and atmospheric pressures. The table was formulated in a laboratory using pure water. The values given are only approximations for estimating the oxygen content of a particular body of surface water.

Table 3 Dissolved Oxygen Saturation In Water

		Pressure in Millimeters and Inches Hg							
		mm							
		775	760	750	725	700	675	650	625
Temp		inches							
°F	°C	30.51	29.92	29.53	28.45	27.56	26.57	25.59	24.61
32.0	0	14.9	14.6	14.4	13.9	13.5	12.9	12.5	12.0
33.8	1	14.5	14.2	14.1	13.6	13.1	12.6	12.2	11.7
35.6	2	14.1	13.9	13.7	13.2	12.9	12.3	11.8	11.4
37.4	3	13.8	13.5	13.3	12.9	12.4	12.0	11.5	11.1
39.2	4	13.4	13.2	13.0	12.5	12.1	11.7	11.2	10.8
41.0	5	13.1	12.8	12.6	12.2	11.8	11.4	10.9	10.5
42.8	6	12.7	12.5	12.3	11.9	11.5	11.1	10.7	10.3
44.6	7	12.4	12.2	12.0	11.6	11.2	10.8	10.4	10.0
46.4	8	12.1	11.9	11.7	11.3	10.9	10.5	10.1	9.8
48.2	9	11.8	11.6	11.5	11.1	10.7	10.3	9.9	9.5
50.0	10	11.6	11.3	11.2	10.8	10.4	10.1	9.7	9.3
51.8	11	11.3	11.1	10.9	10.6	10.2	9.8	9.5	9.1
53.6	12	11.1	10.8	10.7	10.3	10.0	9.6	9.2	8.9
55.4	13	10.8	10.6	10.5	10.1	9.8	9.4	9.1	8.7
57.2	14	10.6	10.4	10.2	9.9	9.5	9.2	8.9	8.5
59.0	15	10.4	10.2	10.0	9.7	9.3	9.0	8.7	8.3
60.8	16	10.1	9.9	9.8	9.5	9.1	8.8	8.5	8.1
62.6	17	9.9	9.7	9.6	9.3	9.0	8.6	8.3	8.0
64.4	18	9.7	9.5	9.4	9.1	8.8	8.4	8.1	7.8
66.2	19	9.5	9.3	9.2	8.9	8.6	8.3	8.0	7.6
68.0	20	9.3	9.2	9.1	8.7	8.4	8.1	7.8	7.5
69.8	21	9.2	9.0	8.9	8.6	8.3	8.0	7.7	7.4
71.6	22	9.0	8.8	8.7	8.4	8.1	7.8	7.5	7.2
73.4	23	8.8	8.7	8.5	8.2	8.0	7.7	7.4	7.1

Table 3 Dissolved Oxygen Saturation In Water (continued)

		Pressure in Millimeters and Inches Hg							
		mm							
		775	760	750	725	700	675	650	625
Temp		inches							
°F	°C	30.51	29.92	29.53	28.45	27.56	26.57	25.59	24.61
75.2	24	8.7	8.5	8.4	8.1	7.8	7.5	7.2	7.0
77.0	25	8.5	8.4	8.3	8.0	7.7	7.4	7.1	6.8
78.8	26	8.4	8.2	8.1	7.8	7.6	7.3	7.0	6.7
80.6	27	8.2	8.1	8.0	7.7	7.4	7.1	6.9	6.6
82.4	28	8.1	7.9	7.8	7.6	7.3	7.0	6.7	6.5
84.2	29	7.9	7.8	7.7	7.4	7.2	6.9	6.6	6.4
86.0	30	7.8	7.7	7.6	7.3	7.0	6.8	6.5	6.2
87.8	31	7.7	7.5	7.4	7.2	6.9	6.7	6.4	6.1
89.6	32	7.6	7.4	7.3	7.0	6.8	6.6	6.3	6.0
91.4	33	7.4	7.3	7.2	6.9	6.7	6.4	6.2	5.9
93.2	34	7.3	7.2	7.1	6.8	6.6	6.3	6.1	5.8
95.0	35	7.2	7.1	7.0	6.7	6.5	6.2	6.0	5.7
96.8	36	7.1	7.0	6.9	6.6	6.4	6.1	5.9	5.6
98.6	37	7.0	6.8	6.7	6.5	6.3	6.0	5.8	5.6
100.4	38	6.9	6.7	6.6	6.4	6.2	5.9	5.7	5.5
102.2	39	6.8	6.6	6.5	6.3	6.1	5.8	5.6	5.4
104.0	40	6.7	6.5	6.4	6.2	6.0	5.7	5.5	5.3
105.8	41	6.6	6.4	6.3	6.1	5.9	5.6	5.4	5.2
107.6	42	6.5	6.3	6.2	6.0	5.8	5.6	5.3	5.1
109.4	43	6.4	6.2	6.1	5.9	5.7	5.5	5.2	5.0
111.2	44	6.3	6.1	6.0	5.8	5.6	5.4	5.2	4.9
113.0	45	6.2	6.0	5.9	5.7	5.5	5.3	5.1	4.8
114.8	46	6.1	5.9	5.9	5.6	5.4	5.2	5.4	4.8
116.6	47	6.0	5.9	5.8	5.6	5.3	5.1	4.8	4.7
118.4	48	5.9	5.8	5.7	5.5	5.3	5.0	4.8	4.6
120.2	49	5.8	5.7	5.6	5.4	5.2	5.0	4.7	4.5
122.0	50	5.7	5.6	5.5	5.3	5.1	4.9	4.7	4.4

Sample Collection, Preservation and Storage

Correct sampling and storage are critical for accurate testing. For greatest accuracy, thoroughly clean sampling devices and containers to prevent carryover from previous samples. Preserve the sample properly; each procedure has information about sample preservation.

- The least expensive containers are polypropylene or polyethylene.
- The best and most expensive containers are quartz or PTFE (polytetrafluoroethylene, Teflon).
- Avoid soft glass containers for metals in the microgram-per-liter range.
- Store samples for silver determination in light-absorbing containers, such as amber bottles.

Avoid contaminating the sample with metals from containers, deionized water or membrane filters. Thoroughly clean sample containers as described under Acid Washing Bottles.

Preservation slows the chemical and biological changes that continue after collection. These processes may change the amount of a chemical species available for analysis. Normally, analyze the samples as soon as possible after collection, especially when the analyte concentration is expected to be low. This also reduces the chance for error and minimizes labor.

Preservation methods include pH control, chemical addition, refrigeration and freezing. *Table 4* gives the recommended preservation for various substances. It also includes suggested types of containers and the maximum recommended holding times for properly preserved samples.

Preserve aluminum, cadmium, chromium, cobalt, copper, iron, lead, nickel, potassium, silver and zinc samples for at least 24 hours by adding one Nitric Acid Solution Pillow 1:1 (Cat. No. 2540-98) per liter of sample. Check the pH with pH indicator paper or a pH meter to assure the pH is 2 or less. Add additional pillows if necessary. Adjust the sample pH prior to analysis by adding an equal number of Sodium Carbonate Anhydrous Powder Pillows (Cat. No. 179-98). Or raise the pH to 4.5 with Sodium Hydroxide Standard Solution, 1 N or 5 N. Correct for the added volume of the preservatives; see *Correcting For Volume Additions.*

Table 4 Required Containers, Preservation Techniques and Holding Times[1]

Parameter No./Name	Container[2]	Preservation[3,4]	Maximum Holding Time[5]
Table 1A - Bacterial Tests:			
1-4. Coliform, fecal and total	P,G	Cool, 4°C, 0.008%, $Na_2S_2O_3$[6]	6 hours
5. Fecal streptococci	P,G	Cool, 4°C, 0.008%, $Na_2S_2O_3$	6 hours
Table 1B - Inorganic Tests:			
1. Acidity	P, G	Cool, 4°C	14 days
2. Alkalinity	P, G	Cool, 4°C	14 days
4. Ammonia	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
9. Biochemical oxygen demand (BOD)	P, G	Cool, 4°C	48 hours
11. Bromide	P, G	None required	28 days
14. Biochemical oxygen demand, carbonaceous	P, G	Cool, 4°C	48 hours
15. Chemical oxygen demand	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
16. Chloride	P, G	None required	28 days
17. Chlorine, total residual	P, G	None required	Analyze immediately
21. Color	P, G	Cool, 4°C	48 hours
23-24. Cyanide, total and amenable to chlorination	P, G	Cool, 4°C, NaOH to pH>12, 0.6 g ascorbic acid[6]	14 days[7]
25. Fluoride	P	None required	28 days
27. Hardness	P, G	HNO_3 to pH<2, H_2SO_4 to pH<2	6 months
28. Hydrogen ion (pH)	P, G	None required	Analyze immediately
31, 43. Kjeldahl and organic nitrogen	P, G	Cool 4°C, H_2SO_4 to pH<2	28 days
Metals:[8]			
18. Chromium VI	P, G	Cool, 4°C	24 hours
35. Mercury	P, G	HNO_3 to pH<2	6 months
3, 5-8, 12, 13, 19, 20, 22, 26, 29, 30, 32-34, 36, 37, 45, 47, 51, 52, 58-60, 62, 63, 70-72, 74, 75.[9] Metals, except boron, chromium VI and mercury	P, G	do	6 months
38. Nitrate	P, G	Cool, 4°C	48 hours
39. Nitrate-nitrite	P, G	Cool 4°C, H_2SO_4 to pH<2	28 days
40. Nitrite	P, G	Cool, 4°C	48 hours
41. Oil and grease	G	Cool, 4°C, HCl or H_2SO_4 to pH<2	28 days
42. Organic Carbon	P, G	Cool, 4°C, HCl or H_2SO4 or H_3PO_4 to pH<2	28 days
44. Orthophosphate	P, G	Filter immediately; Cool, 4°C	48 hours
46. Oxygen, dissolved probe	G Bottle and top	None required	Analyze immediately
47. Winkler	G Bottle and top	Fix on site and store in dark	8 hours

Table 4 Required Containers, Preservation Techniques and Holding Times[1] (continued)

Parameter No./Name	Container[2]	Preservation[3,4]	Maximum Holding Time[5]
48. Phenols	G only	Cool 4°C, H_2SO_4 to pH<2	28 days
49. Phosphorus, elemental	G	Cool, 4°C	48 hours
50. Phosphorus, total	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
53. Residue, total	P, G	Cool, 4°C	7 days
54. Residue, filterable	P, G	Cool, 4°C	7 days
55. Residue, Nonfilterable (TSS)	P, G	Cool, 4°C	7 days
56. Residue, Settleable	P, G	Cool, 4°C	48 hours
57. Residue, volatile	P, G	Cool, 4°C	7 days
61. Silica	P, PFTE or quartz	Cool, 4°C	28 days
64. Specific conductance	P, G	Cool, 4°C	28 days
65. Sulfate	P, G	Cool, 4°C	28 days
66. Sulfide	P, G	Cool 4°C, add zinc acetate plus sodium hydroxide to pH>9	7 days
67. Sulfite	P, G	none required	Analyze immediately
68. Surfactants	P, G	Cool, 4°C	48 hours
69. Temperature	P, G	None required	Analyze immediately
73. Turbidity	P, G	Cool, 4°C	48 hours

1 This table was taken from Table II published in the Federal Register, July 1, 1995, 40 CFR, Part 136.3, pages 643-645. Organic tests are not included.

2 Polyethylene (P) or glass (G).

3 Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

4 When any sample is to be shipped by common carrier or sent through United States Mails, it must comply with the Department of Transportation Hazardous Material Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

5 Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permitee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time, and has received a variance from the Regional Administer under §136.3(e). Some samples may not be stable for the maximum time period given in the table. A permitee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show that this is necessary to maintain sample stability. See §136.3(e) for details. The term “analyze immediately” usually means within 15 minutes or less after sample collection.

6 Should only be used in the presence of residual chlorine.

7 Maximum holding time is 24 hours when sulfide is present. Optionally all samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

8 Samples should be filtered immediately on-site before adding preservative for dissolved metals.

9 Numbers refer to parameter numbers in 40 CFR Part 136.3, Table 1B.

Collecting Water Samples

Obtain the best sample by careful collection. In general, collect samples near the center of the vessel or duct and below the surface. Use only clean containers (bottles, beakers). Rinse the container several times first with the water to be sampled.

Take samples as close as possible to the source of the supply. This lessens the influences of the distribution system on the sample. Let the water run long enough to flush the system. Fill sample containers slowly with a gentle stream to avoid turbulence and air bubbles. Collect water samples from wells after the pump has run long enough to deliver water representative of the ground water feeding the well.

It is hard to obtain a truly representative sample when collecting surface water samples. Obtain best results by testing several samples. Use samples taken at different times from several locations and depths. The results can be used to establish patterns for that particular body of water.

Generally, as little time as possible should elapse between collecting the sample and analyzing it.

Depending on the test, special precautions in handling the sample may be necessary. This prevents natural interferences such as organic growth or loss or gain of dissolved gases. Each procedure describes sample preservatives and storage techniques for samples that are held for testing.

Acid Washing Bottles

If a procedure suggests acid-washing, use the following instructions:

a) Clean the glassware or plasticware with laboratory detergent (phosphate-free detergent is recommended).

b) Rinse well with tap water.

c) Rinse with a 1:1 Hydrochloric Acid Solution or 1:1 Nitric Acid Solution.

d) Rinse well with deionized water at least four times. Up to 12-15 rinses may be necessary if chromium is being determined.

e) Air dry.

Use chromic acid or chromium-free substitutes to remove organic deposits from glass containers. Rinse containers thoroughly with water to remove traces of chromium.

Wash glassware for phosphate determinations with phosphate-free detergents and acid-wash with 1:1 HCl. Thoroughly rinse the glassware with deionized water. For ammonia and Kjeldahl nitrogen, rinse with ammonia-free water.

Correcting for Volume Additions

If you use a large volume of preservative, correct for the volume of preservative added. This accounts for dilution due to the acid added to preserve the sample and the base used to adjust the pH to the range of the procedure. This correction is made as follows:

1. Determine the volume of initial sample, the volume of acid and base added, and the total or final volume of the sample.

2. Divide the total volume by the initial volume of sample.

3. Multiply the test result by this factor.

Example:

A one-liter sample was preserved with 2 mL of nitric acid. It was neutralized with 5 mL of 5 N sodium hydroxide. The result of the analysis procedure was 10.00 mg/L. What is the volume correction factor and correct result?

1. Total Volume = 1000 mL + 2 mL + 5 mL = 1007 mL

2. $\frac{1007}{1000} = 1.007$ = volume correction factor

3. $10.0 \text{ mg/L} \times 1.007 = 10.07 \text{ mg/L}$ = correct result

Hach 1:1 Nitric Acid Pillows contain 2.5 mL of acid; correct for this volume. The addition of a Sodium Carbonate Power Pillow (neutralizes the 1:1 Nitric Acid Solution Pillow) does not need to be corrected for.

Boiling Aids

Boiling is necessary in some procedures. Using a boiling aid such as boiling chips (Cat. No. 14835-31) helps reduce bumping. Bumping is caused by the sudden, almost explosive conversion of water to steam as it is heated. Avoid bumping; it may cause injury or sample loss.

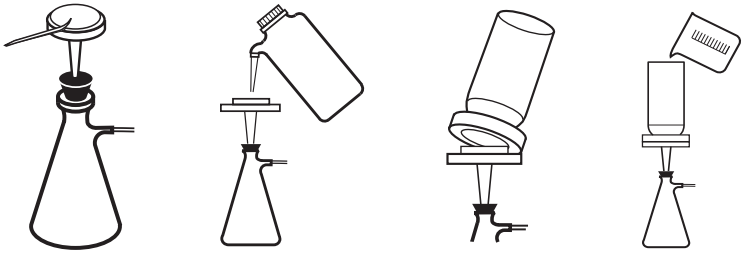
Make sure the boiling aids will not contaminate the sample. Do not use boiling aids (except glass beads) more than once. Loosely covering the sample during boiling will prevent splashing, reduce the chances of contamination and minimize sample loss.

Sample Filtration

Filtering separates particles from the aqueous sample. Filtration uses a medium, usually filter paper, to retain particles but pass solution. This is especially helpful when sample turbidity interferes with analysis. Two general methods of filtration are gravity and vacuum. Gravity filtration uses gravity to pull the sample though the filter paper. Vacuum filtration uses suction and gravity to move the sample through the filter. An aspirator or vacuum pump creates the suction. Vacuum filtration is faster than gravity filtration. Vacuum filter (see *Figure 1*) as follows:

1. Using tweezers, place a filter paper into the filter holder.
2. Place the filter holder assembly in the filtering flask. Wet the filter with deionized water to ensure adhesion to the holder. Empty the flask before filtering the sample.
3. Position the funnel housing on the filter holder assembly.
4. While applying a vacuum to the filtering flask, transfer the sample to the filtering apparatus.
5. Slowly release the vacuum from the filtering flask and transfer the solution from the filter flask to another container.

Figure 1 Vacuum Filtration



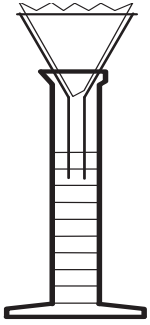
REQUIRED APPARATUS FOR VACUUM FILTRATION

Description	Unit	Cat. No.
Filter Discs, glass 47 mm, 1.5 µm	100/pkg	2530-00
Filter Holder, membrane	each	13529-00
Flask, filter, 500 mL	each	546-49
Pump, vacuum, hand operated	each	14283-00
OR		
Pump, vacuum, portable, 115 V	each	14697-00
Pump, vacuum, portable, 230 V	each	14697-02

Several procedures in this manual use gravity filtration. The only labware required is filter paper, a conical funnel and a receiving vessel. This labware is included under Optional Apparatus at the end of a procedure. Gravity filtration is better for retaining fine particles. For faster filtering, add solution until the filter paper cone is three-fourths filled. Never fill the cone completely. Gravity filter (see *Figure 2*) as follows:

1. Place a filter paper into the funnel.
2. Wet the filter with deionized water to ensure adhesion to the funnel. Allow all the deionized water to drain.
3. Place the funnel into an erlenmeyer flask or graduated cylinder.
4. Pour the sample into the funnel.

Figure 2 Gravity Filtration



REQUIRED APPARATUS FOR GRAVITY FILTRATION

Description	Unit	Cat No.
Cylinder, graduated, 100 mL	each	508-42
Funnel, poly, 65 mm	each	1083-67
Filter Paper, 12.5 cm	each	1894-57
Flask, erlenmeyer, 125 mL	each	505-43

Testing for metals requires acid and heat to pretreat the sample. Since these conditions destroy filter paper, vacuum filtration with glass fiber filter discs is recommended. Also, glass filter discs, unlike paper, do not retain colored species.

Temperature Considerations

For best results, perform most tests in this manual with sample temperatures between 20 °C (68 °F) and 25 °C (77 °F). If a test requires closer temperature control, notes in the procedure will indicate this.

Sample Dilution Techniques

Ten and 25 mL are the volumes used for most colorimetric tests. However, in some tests, the color developed in the sample may be too intense to be measured. Unexpected colors may develop in other tests. In both cases, dilute the sample to determine if interfering substances are present.

To dilute the sample easily, pipet the chosen sample portion into a clean graduated cylinder (or volumetric flask for more accurate work). Fill the cylinder (or flask) to the desired volume with deionized water. Mix well. Use the diluted sample when running the test.

To help with dilutions, *Table 5* shows the amount of sample used, the amount of deionized water used to bring the volume up to 25 mL and the multiplication factor.

The concentration of the sample is equal to the diluted sample reading multiplied by the multiplication factor.

More accurate dilutions can be done with a pipet and a 100-mL volumetric flask (see *Table 6* for more information). Pipet the sample and dilute to volume with deionized water. Swirl to mix.

Table 5 Sample Dilution Volumes

Sample Volume (mL)	mL Deionized Water Used to Bring the Volume to 25 mL	Multiplication Factor
25.0	0.0	1
12.5	12.5	2
10.0[1]	15.0	2.5
5.0[1]	20.0	5
2.5[1]	22.5	10
1.0[1]	24.0	25
0.250[1]	24.75	100

[1] For sample sizes of 10 mL or less, use a pipet to measure the sample into the graduated cylinder or volumetric flask.

Table 6 Multiplication Factors for Diluting to 100 mL

Sample Volume (mL)	Multiplication Factor
1	100
2	50
5	20
10	10
25	4
50	2

Sample Dilution and Interfering Substances

Sample dilution may influence the level at which a substance may interfere. The effect of the interferences decreases as the dilution increases. In other words, higher levels of an interfering substance can be present in the original sample if it is diluted before analysis.

An Example:

Copper does not interfere at or below 100 mg/L for a 25.00 mL sample in a procedure. If the sample volume is diluted with an equal volume of water, what is the level at which copper will not interfere?

$$\frac{\text{Total volume}}{\text{Sample volume}} = \text{Dilution factor}$$

$$\frac{25}{12.5} = 2$$

$$\text{Interference Level} \times \text{Dilution Factor} = \text{Interference level in sample}$$

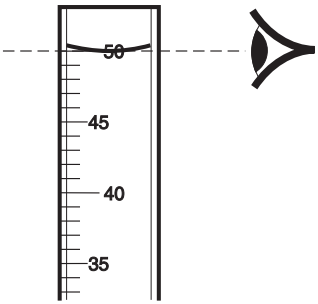
$$100 \times 2 = 200$$

The level at which copper will not interfere in the undiluted sample is at or below 200 mg/L.

Using Pipets and Graduated Cylinders

When small sample quantities are used, the accuracy of measurements is important. *Figure 3* illustrates the proper way of reading the sample level or the meniscus formed when the liquid wets the cylinder or pipet walls.

Figure 3 Reading the Meniscus



Rinse the pipet or cylinder two or three times with the sample to be tested before filling. Use a pipet filler or pipet bulb to draw the sample into the pipet. Never pipet chemical reagent solutions or samples by mouth. When filling a pipet, keep the tip of the pipet below the surface of the sample as the sample is drawn into the pipet.

Serological pipets have marks that indicate the volume of liquid delivered by the pipet. The marks may extend to the tip of the pipet or may be only on the straight portion of the tube. If the marks are only on the straight part of the tube, fill serological pipets to the zero mark and discharge the sample by draining the sample until the meniscus is level with the desired mark. If the serological pipet has marks extended to the tip of the pipet, fill the pipet to the desired volume and drain all the sample from the pipet. Then blow the sample out of the pipet tip for accurate measurements.

Volumetric (transfer) pipets have a bulb in the middle and a single ring above the bulb to indicate the volume of liquid when it is filled to the mark. To discharge a volumetric pipet, hold the pipet vertical until only a small amount of liquid remains (about ¾ inch), then hold the pipet at a slight angle against the container wall to drain. Do not attempt to discharge the solution remaining in the tip of the pipet after draining. Volumetric pipets are designed to retain a small amount of sample in the pipet tip.

If sample drops stay on the walls of the pipet, the pipet is dirty and is not delivering the correct amount of sample. Wash the pipet thoroughly with a laboratory detergent or cleaning solution and rinse several times with deionized water.

Using the TenSette Pipet

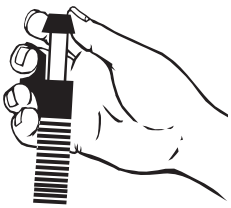
For best results use a new tip each time you pipet. After several uses, the pipet tip may retain some liquid, causing inaccurate delivery. Each pipet is supplied with 50 tips; order Hach replacement tips for best results.

Always use careful, even hand movements for best reproducibility. If the pipet does not operate smoothly, disassemble and coat the piston and retainer with high-quality stopcock grease. Also coat the metering turret lightly with grease. Refer to the TenSette Pipet manual.

For best pipetting accuracy, the solution and the room temperature should be between 20-25 °C.

Never lay the pipet down with the liquid in the tip. Solution could leak into the pipet and cause corrosion.

Operating the TenSette Pipet



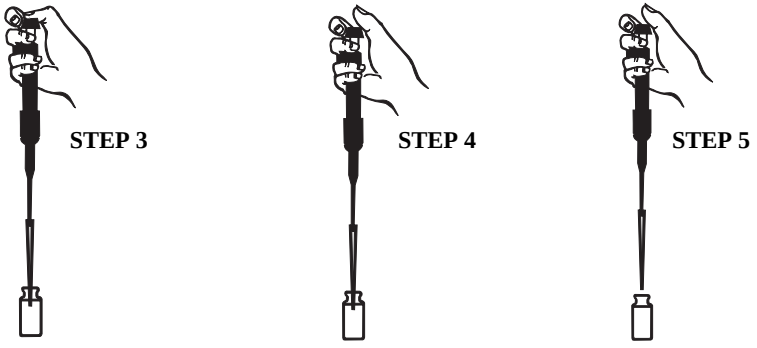
1. Attach a clean tip by holding the pipet body in one hand and gently pressing the large end of the pipet tip onto the tapered end of the pipet. Be sure a good seal is obtained.

2. Turn the turret cap to align the desired volume with the mark on the pipet body.

3. Using a smooth motion, press down on the turret cap until it reaches the stop. Immerse the tip about 5 mm (¼ inch) below the solution surface to avoid drawing air into the pipet. Do not insert the tip any deeper or the delivery volume may be affected.

4. While maintaining a constant pressure, allow the turret to return slowly to the extended position. A rapid return may affect the delivery volume.

5. With the turret up, take the tip out of the solution and move it to the receiving vessel. Do not press on the turret cap while moving the pipet.




STEP 6

6. Use the thumb and forefinger to twist the turret cap to the next higher volume position to ensure quantitative transfer of the sample. The “F” position provides full blowout.


STEP 7

7. With the tip in contact with the side of the receiving vessel, slowly and smoothly press down on the turret cap until it reaches the stop and the solution is completely discharged.

Mixing Water Samples

The following two methods may be helpful in tests that require mixing sample with chemicals (usually indicated by "invert to mix" instructions).

1. When mixing sample in a round sample cell or mixing cylinder, invert the cell or cylinder; see *Figure 4*. Hold the cell in a vertical position with the cap on top. Invert the cell so the cap is on the bottom. Return the cell to the original position. Do the same with the mixing cylinder.

2. Swirling is recommended when mixing samples in a graduated cylinder or a titration flask. Grip the cylinder (or flask) firmly with the tips of three fingers; see *Figure 5*. Hold the cylinder at a 45-degree angle and twist the wrist. This should move the cylinder in an approximately 12-inch circle, creating enough rotation to complete the mixing in a few turns.

These mixing procedures are the most gentle. Both methods are simple but take a bit of practice to obtain the best results.

Figure 4 Inverting a Sample Cell

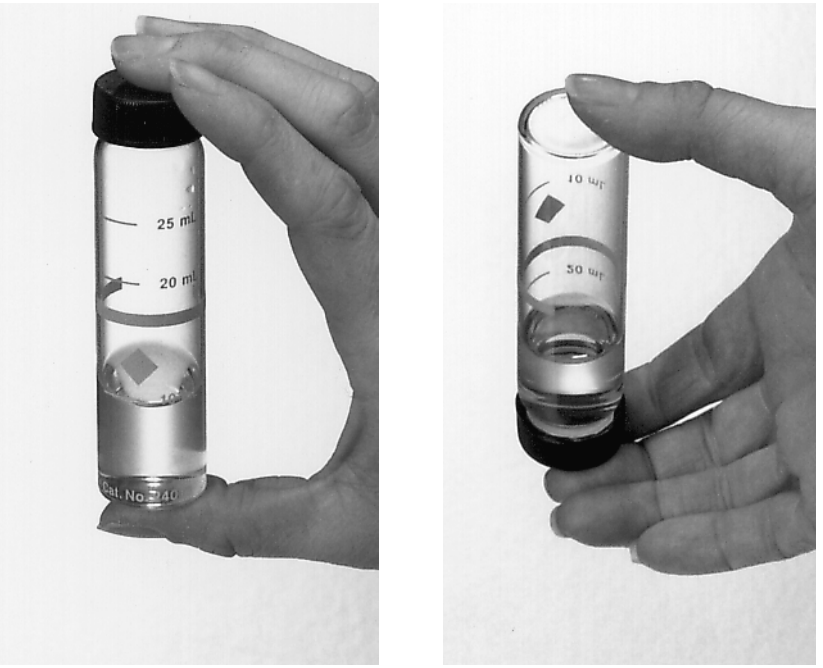
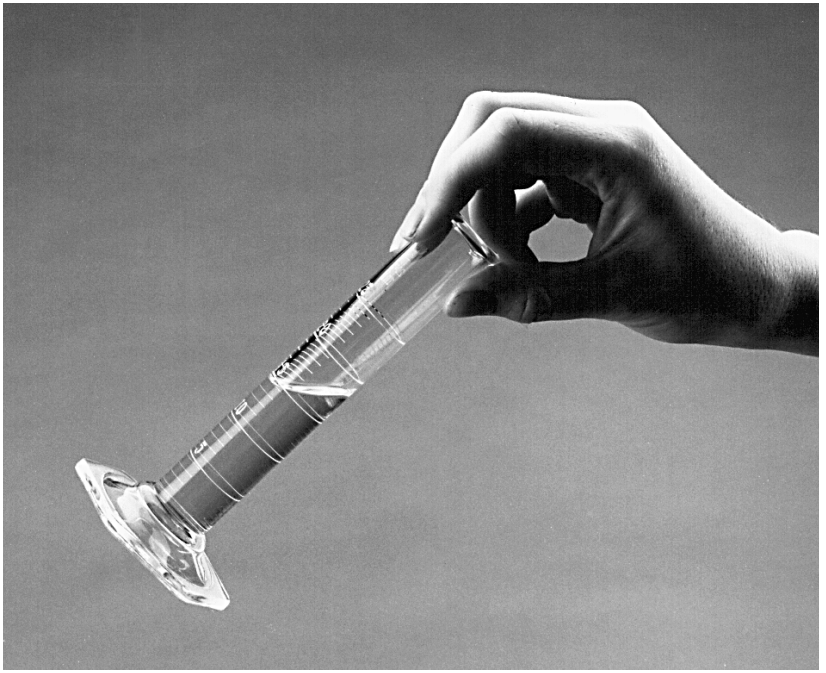


Figure 5 Swirling a Graduated Cylinder



Using Sample Cells

Orientation of Sample Cells

Two round sample cells are shipped with the DR/820, DR/850 and DR/890. They are marked with 10-, 20- and 25-mL fill lines which may be used to measure the sample volume unless the procedure instructs you to use other glassware to measure the sample volume.

To minimize variability of measurements using a particular cell, always place the cell into the cell holder with the same orientation. The cells are placed in the instrument with the fill marks facing the user.

In addition to proper orientation, the sides of the cells should be free of smudges, fingerprints, etc. to ensure accurate readings. Wipe the sides of the cells with a moist cloth followed by a dry soft cloth to clean the surface before taking measurements.

Care of Hach Sample Cells

Store sample cells in their boxes when not in use to protect them from scratching and breaking. It is good laboratory practice to empty and clean sample cells after analyses are complete--avoid leaving colored solutions in the cells for extended periods of time. Finish the cleaning procedure with a few rinses of deionized water and allow to dry. Individual procedures often recommend specific cleaning methods.

Cleaning Sample Cells

Most laboratory detergents can be used at recommended concentrations. Neutral detergents such as Neutracon are safer if regular cleaning is required, as in the case of protein residues.

If using a detergent, you can speed cleaning by increasing the temperature or using an ultrasonic bath.

Rinsing is more efficient when using deionized water.

Using the COD/TNT Adapter

Use care when seating a vial into the COD/ TNT adapter (for COD vials and Test ‘N Tubes). Place the vial into the adapter and press straight down on the top of the vial until it seats solidly. Do not move the vial from side to side; this can cause errors.

Volume Measurement Accuracy

The sample cells supplied with the instrument have fill marks to indicate 10, 20 or 25 mL. The fill marks are intended to measure the volume to be analyzed. Do not use these fill marks to perform sample dilutions.

If a sample must be diluted, use a pipet, graduated mixing cylinder and/or a volumetric flask for accurate measurement. When diluting, accuracy is important because a slight mistake in measuring a small sample will cause

a substantial error in the result. For instance, a 0.1-mL mistake in the dilution of a 1.0-mL final volume produces a 10% error in the test result.

Volumes for standard additions can be measured using the 25-mL mark, but it is not recommended for the 10-mL mark due to a potentially excessive relative error. An error of 0.5 mL in 25 mL is only 2%, while 0.5 mL error in 10 mL is 5%.

For 10 mL standard additions, follow this procedure:

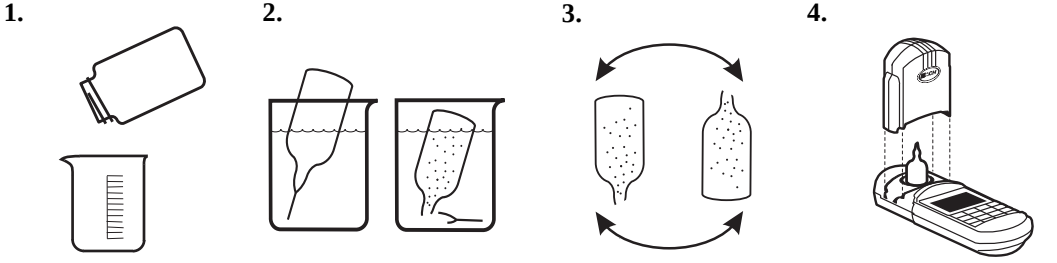
1. Transfer 10.0 mL of sample into a clean, dry sample cell (the unspiked sample).
2. Add the standard (spike) to a 25 mL portion of sample in a 25-mL mixing cylinder. Stopper and mix thoroughly.
3. Transfer 10 mL to another sample cell (use fill mark) for analysis.

Using AccuVac Ampuls

AccuVac ampuls contain pre-measured powder or liquid in optical-quality glass ampuls.

1. Collect the sample in a beaker or other open container.
2. Place the ampul tip well below the sample surface and break the tip off (see *Figure 6*) against the beaker wall. The break must be far enough below the surface to prevent air from being drawn in as the level of the sample lowers (the AccuVac Breaker may be used instead of breaking the ampul against the beaker side).
3. Invert the ampul several times to dissolve the reagent. Do not place your finger over the broken end; the liquid will stay in the ampul when inverted. Wipe the ampul with a towel to remove fingerprints, etc.
4. Insert the ampul into the instrument and read the results directly.

Figure 6 Using AccuVac Ampuls



Using Reagent Powder Pillows

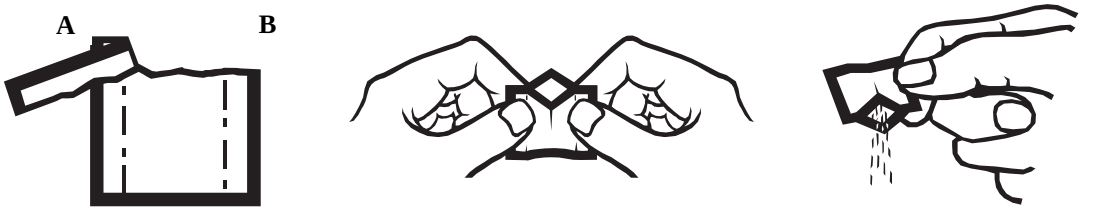
Hach uses dry powdered reagents when possible. This minimizes leakage and deterioration problems. Some powders are packaged in individual, pre-measured, polyethylene "powder pillows" or foil pillows called PermaChem® pillows. Each pillow contains enough reagent for one test. Open the poly powder pillows with nail clippers or scissors; see *Figure 7*.

Figure 7 Opening Powder Pillows

Using PermaChem Pillows

1. Tap the pillow on a hard surface to collect the powdered reagent in the bottom.
2. Tear (or cut) across the top of the pillow, from B to A, holding the pillow away from your face.
3. Using two hands, push both sides toward each other to form a spout.
4. Pour the pillow contents into the sample cell and continue the procedure according to the instructions. Tap the pillow to remove any powder from the corners.

1. Tear **2. Push** **3. Pour**



Reagent and Standard Stability

Hach always strives to make stable formulations and package them to provide maximum protection. Most chemicals and prepared reagents do not deteriorate after manufacture. However, the way they are stored and the packaging can affect how long the reagents are stable. Light, bacterial action, and absorption of moisture and gases from the atmosphere can affect shelf life. Some chemicals may react with the storage container or they may react with other chemicals.

Chemicals supplied with the colorimeter have an indefinite shelf life when stored under average room conditions, unless the packaging says something different. Product labels state any special storage conditions required. Otherwise, store reagents in a cool, dry, dark place for maximum life. It is always good practice to date chemicals when you receive them. Use older supplies first. If in doubt about the reagent shelf life, run a standard to check its effectiveness.

Interferences

Substances in the sample may interfere with a measurement. Hach mentions common interferences in the test procedures. The reagent formulations eliminate many interferences. You can remove others with sample pretreatments described in the procedure.

If you get an unusual answer, a color that you don't expect, or you notice an unusual odor or turbidity, the result may be wrong. Repeat the test on a sample diluted with deionized water; see *Sample Dilution Techniques*. Compare the result (corrected for the dilution) with the result of the original test. If these two are not close, the original result may be wrong and you should make an additional dilution to check the second test (first dilution). Repeat this process until you get the same corrected result twice in a row.

More information about interferences and methods to overcome them is contained in *Standard Additions* of this manual and the *General Introduction* section of APHA Standard Methods. Hach urges the analyst to obtain this book and refer to it when problems are encountered.

One of the greatest aids is knowing what is in the sample. You don't need to know exactly what is in each sample, but be aware of substances that are likely to interfere in the analysis method you use. When using a method, it may be helpful to determine if those interferences are present.

pH Interference

Many of the procedures in this manual only work within a certain pH range. Hach reagents contain buffers to adjust the pH of the typical sample to the correct pH range. However, the reagent buffer may not be strong enough for some samples. This occurs most often with highly buffered samples or samples with extreme sample pH.

The *Sampling and Storage* section of each procedure usually gives the proper pH range for the sample.

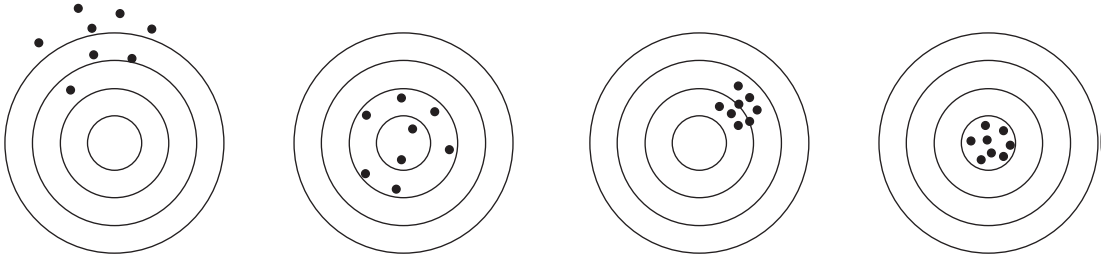
Adjust the sample to the proper pH range before testing. If this information is not given, follow these steps:

1. Measure the pH of your analyzed sample with a pH meter. For measuring Ag^+, K^+ or Cl^- , use pH paper.
2. Prepare a sample using deionized water. Add all reagents called for in the procedure. Timer sequences, etc., may be ignored. Mix well.
3. Measure the pH of the reagent blank with a pH meter.
4. Compare the pH values of your analyzed sample with the reagent blank.
5. If there is little difference in the values of your analyzed sample and the reagent blank, then pH interference is not the problem. Follow the *Accuracy Check* given in the procedure to help identify the problem.
6. If there is a large difference between the value of your analyzed sample and the reagent blank, adjust the sample pH to the value of the reagent blank. Adjust the sample pH to this same pH for all future samples from the same source before analysis. Use the appropriate acid, usually nitric acid, to lower the pH (do not use nitric acid for nitrate or nitrogen testing). Use the appropriate base, usually sodium hydroxide, to raise the pH. Adjust the final result for any dilution caused by adding acid or base; see *Correcting for Volume Additions*.
7. Analyze the sample as before.
8. Some purchased standards may be very acidic and will not work directly with Hach procedures. Adjust the pH of these standards as described above. Adjust the final concentration of the standard for the dilution. The Hach standard solutions suggested in the procedures are formulated so that no pH adjustment is necessary.

Accuracy and Precision

Accuracy is the nearness of a test result to the true value. Precision is how closely repeated measurements agree with each other. Although good precision suggests good accuracy, precise results can be inaccurate (see *Figure 8*). The following paragraphs describe how to improve accuracy and precision of analyses by using Standard Additions.

Figure 8 Precision and Accuracy Illustrated



Standard Additions

Standard Additions is a common technique for checking test results. Other names are “spiking” and “known additions.” The standard additions technique can test for interferences, bad reagents, faulty instruments, and incorrect procedures.

Perform Standard Additions by following the Standard Additions Method section in the procedure under *Accuracy Check*. Follow the detailed instructions given.

If you get about 100% recovery for each addition, everything is working right and your results are correct.

If you don’t get about 100% recovery for each addition, a problem exists. You can tell if you have an interference. Repeat the Standard Additions using deionized water as your sample. If you get about 100% recovery for each addition, you have an interference. If you didn’t get good recoveries with the deionized water, the following checklist may help to find the problem quickly:

1. Check to see that you are following the procedure exactly:

a) Are you using the proper reagents in the proper order? Are you using 10-mL reagents with a 10-mL sample or 25-mL reagents with a 25-mL sample?

b) Are you waiting the necessary time for color to develop?

c) Are you using the correct glassware?

d) Is the glassware clean?

e) Does the test need a specific sample temperature?

f) Is the sample's pH in the correct range?

Hach's written procedure should help you to answer these questions.

2. Check your reagents. Repeat the Standard Additions using new, fresh reagents. If your results are good, the original reagents were bad.

3. If nothing else is wrong, the standard is almost certainly bad. Repeat the Standard Additions with a new standard.

If the check list does not determine the problem, use the decision tree (*Figure 9*) and explanation of each branch, below, to identify the problem.

Branch A

Suppose a single standard addition to the sample did not give the correct concentration increase. A possible cause could be interferences. Other causes include defective reagents, incorrect technique, a defective instrument/apparatus or defective standard used for the standard addition.

If interferences are known or assumed to be absent, proceed to Branch B. If interferences are known to be present, proceed to Branch C.

Branch B

Perform multiple standard additions on a sample of deionized water as in the following example using iron as the analyte of interest:

1. Pour 25 mL of deionized water into a 25-mL sample cell.

2. Add 0.1 mL of a 50-mg/L iron standard solution to a second 25 mL sample of deionized water.

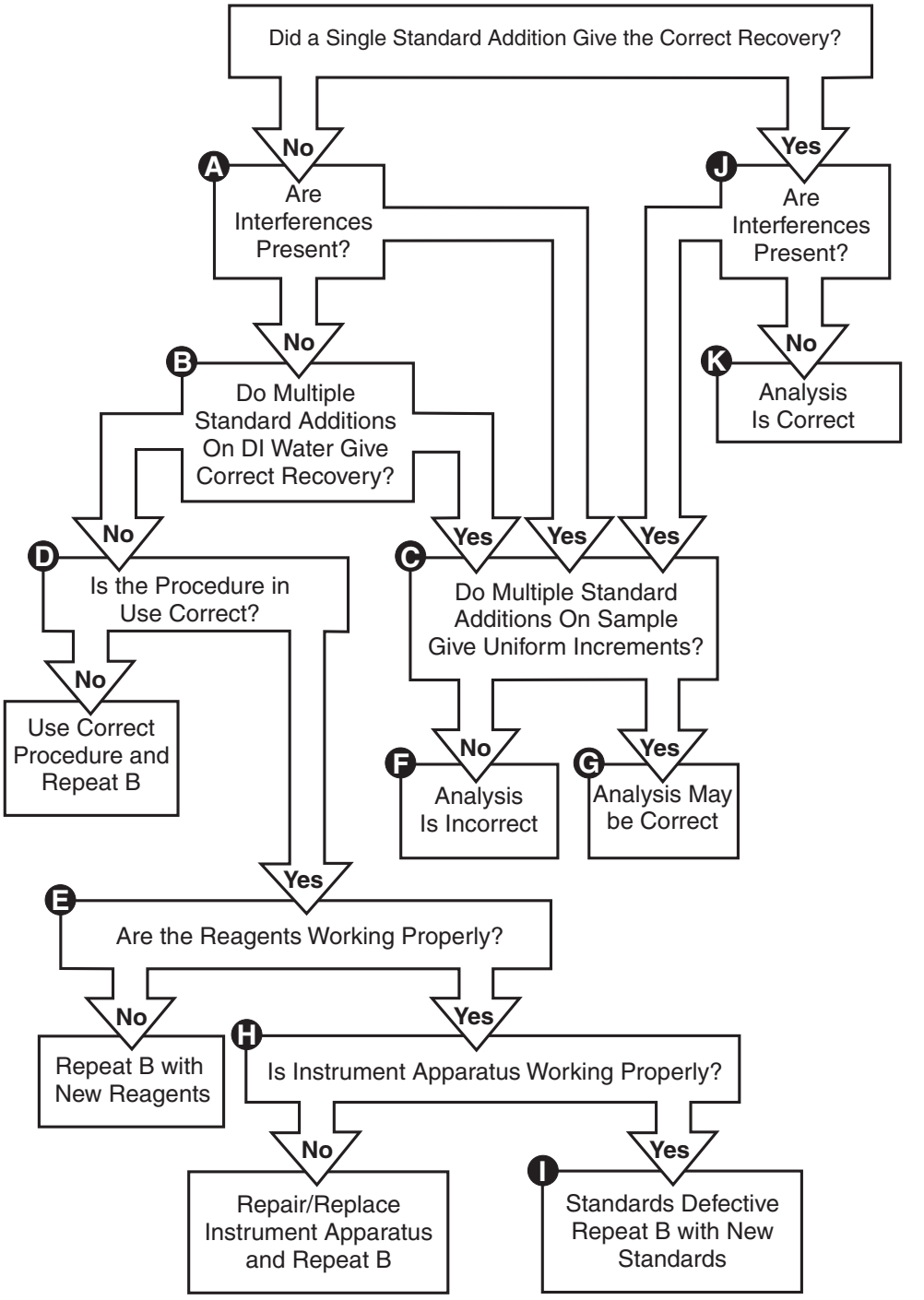
3. Add 0.2 mL of the same standard to a third 25 mL sample of deionized water.

4. Add 0.3 mL of the same standard to a fourth 25 mL sample of deionized water. Analyze all these samples for iron.

5. Tabulate the data as shown below:

mL of Standard Added	mg/L of Standard Added	mg/L of Iron Found
0	0	0
0.1	0.2	0.2
0.2	0.4	0.4
0.3	0.6	0.6

Figure 9 Standard Additions Decision Tree



The data show several points:

- The chemicals, instrument, procedure/technique and standards are working correctly because the iron added to the water sample was completely recovered in the same uniform steps that match the standard addition increments.
- Because iron added to the deionized water was recovered, but iron added to an actual sample was not recovered (Branch A), the sample contains an interference which prevents the test reagents from working properly.
- An iron analysis previously done on the actual sample using this method gave an inaccurate result.

If the results of multiple standard additions give the correct increment for each addition, proceed to Branch C.

If the results of multiple standard additions do not give the correct increment for each addition, go to Branch D.

Branch C

If interfering substances are present, the analysis may be incorrect. However, with multiple standard additions, it may be possible to arrive at an approximate result if the increases are uniform.

Suppose the sample result for iron was 1.0 mg/L. Because interferences may be present, a standard addition of 0.1 mL of a 50 mg/L iron standard to a 25 mL sample is made. The expected increase in the iron concentration is 0.2 mg/L, but the actual increase is 0.1 mg/L. Then 0.2 and 0.3 mL of the same standard are added to two more 25 mL samples and analyzed for iron.

If there is a uniform increase in concentration between each addition (i.e., 0.1 mg/L difference between each addition), use Branch G. If the increase in concentration is not uniform (i.e., 0.1, 0.08, 0.05), go to Branch F.

Branch D

Carefully check the instructions for the test. Make sure to use the correct reagents in the correct order. Be sure the glassware in use is what is required. Be sure time for color development and the sample temperature are as specified. If the procedure technique was incorrect, repeat Branch B. If the procedure was correctly followed, proceed to Branch E.

Branch E

Check the reagent performance. This may be done by obtaining a fresh lot of reagent or by using a known standard solution to run the test. Make sure the color development time given in the procedure is equal to the

time required for the reagent in question. If the reagent(s) is defective, repeat Branch B with new reagents. If the reagents are good, proceed with Branch H.

Branch F

Examples of non-uniform increments between standard additions are shown below.

Example A

mL of Standard Added	mg/L Standard Added	mg/L Found
0	0	1.0
0.1	0.2	1.10
0.2	0.4	1.18
0.3	0.6	1.23

Example B

mL of Standard Added	mg/L Standard Added	mg/L Found
0	0	0
0.1	0.2	0
0.2	0.4	0.2
0.3	0.6	0.4

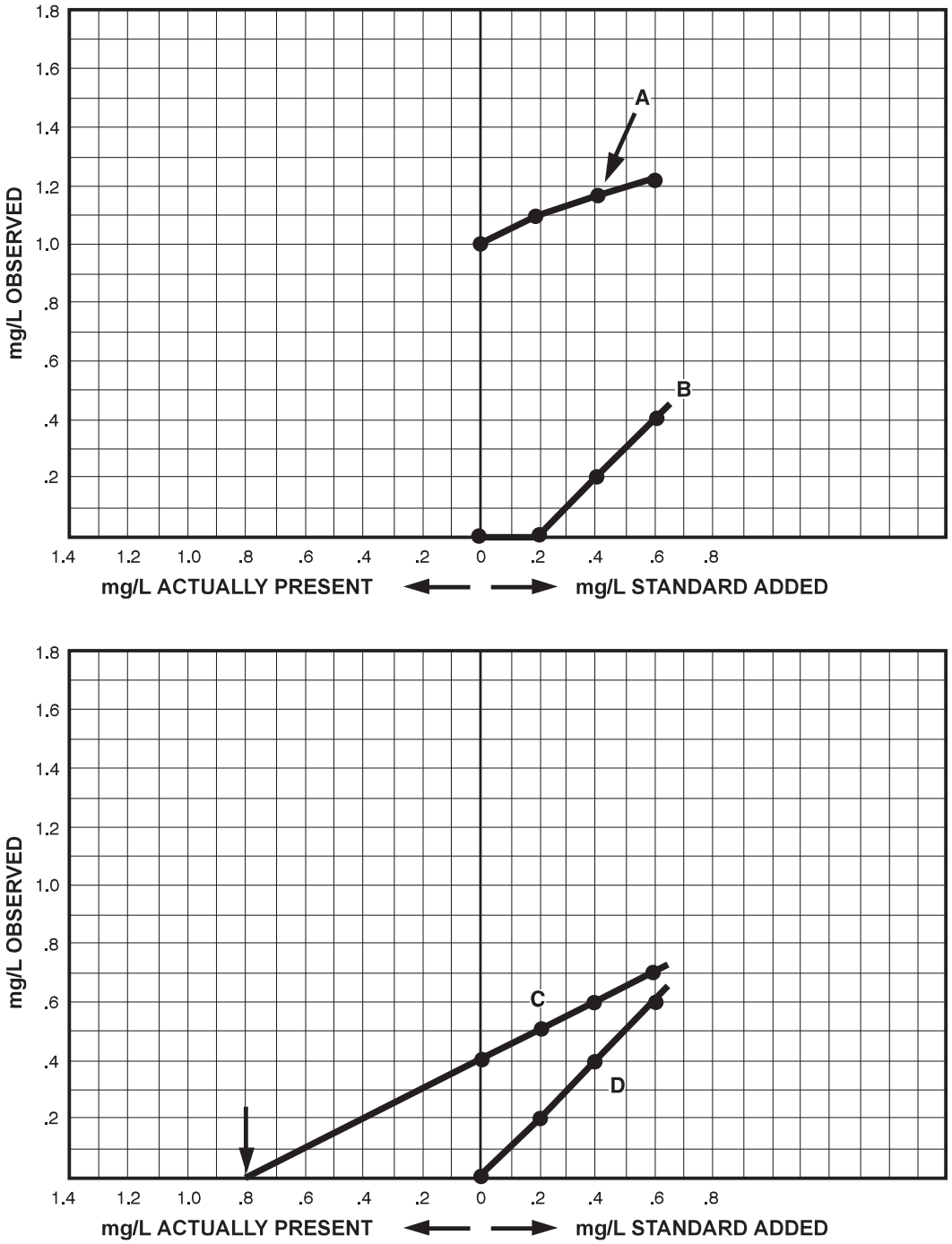
These examples show the effect of interferences on the standard addition. Data plotted on the graph in *Figure 10* for samples A and B show that the four data points do not lie on a straight line.

The plot for sample A illustrates an interference that becomes progressively worse as the concentration of the standard increases. This type of interference is uncommon and may be caused by an error or malfunction of the procedure, reagents or instrument. It is recommended Branch B be performed to verify the supposed interference.

The plot for sample B shows a common chemical interference which becomes less or even zero as the concentration of standard increases. The graph shows the first addition was consumed by the interference and the remaining additions gave the correct increment of 0.2 mg/L.

The apparent interference in Example B could be the result of an error made in the standard addition. Repeat the analysis to see if an error was made during standard addition. If not, the method is not appropriate for the sample matrix. When these two types of interferences occur, try to analyze the sample with a method which uses a different type of chemistry.

Figure 10 Multiple Standard Additions Graph



Branch G

Examples of uniform increments between standard additions are given below.

Example C

mL of Standard Added	mg/L Standard Added	mg/L Found
0	0	0.4
0.1	0.2	0.5
0.2	0.4	0.6
0.3	0.6	0.7

The plot for sample C illustrates a common interference with a uniform effect on the standard and the substances in the sample. The four data points form a straight line which may be extended back through the horizontal axis. The point where the line meets the axis can be used to determine the concentration of the substance you are measuring.

In this example, the first analysis gave 0.4 mg/L. After extrapolating the line to the horizontal axis, the graph shows the result should be much closer to the correct result: 0.8 mg/L.

Apparent interferences may also be caused by a defect in the instrument or standards. Before assuming the interference is chemical, check Branch B.

Example D

mL of Standard Added	mg/L Standard Added	mg/L Found
0	0	0
0.1	0.2	0.2
0.2	0.4	0.4
0.3	0.6	0.6

The plot for sample D illustrates a problem for the analyst. The increments are uniform and the recovery of the standard was complete. The result of the first analysis was 0 mg/L and the line extrapolates back through 0 mg/L. If interferences are known to be present, the interferences may be present in an amount equal to the substance in question, preventing the analyst from finding the substance. This would be an uncommon situation.

Branch H

Check operation of the instrument and/or apparatus used to perform the test. Check glassware used in the procedure and make sure it is extremely clean. Dirty pipets and graduated cylinders can cause contamination and will not deliver the correct volume. Check delivery of pipets by using deionized water and a balance; 0.2 mL = 0.2 grams.

If a defect is found in the instrument and/or apparatus, repeat Branch B after repair or replacement. If the instrument and apparatus are working, proceed with Branch I.

Branch I

After determining the procedure, reagents, instrument and/or apparatus are correct and working properly, you may conclude the only possible cause for standard additions not functioning correctly in deionized water is the standard used for performing standard additions. Obtain a new standard and repeat Branch B.

Branch J

If the standard additions gives the correct result, the analyst must then determine if an interfering substance(s) is present. If interfering substances are present, proceed to Branch C. If they are not present, the analysis is correct.

If you still cannot identify the problem, extra help is available. Please call our Technical Support Group at 800-227-4224 (U.S.A.) or 970-669-3050. A representative will be happy to help you.

Method Performance

Estimated Detection Limit

Ranges for chemical measurements have limits. The lower limit is important because it determines whether a measurement is different from zero. Many experts disagree about the definition of this detection limit, and determining it can be difficult. The Code of Federal Regulations (40 CFR, Part 136, Appendix B) provides a procedure to determine the "Method Detection Limit" or MDL. The MDL is the lowest concentration that is different from zero with a 99% level of confidence. A measurement below this MDL may be useful, but there is a greater chance that it is actually zero.

The MDL is not fixed; it varies for each reagent lot, instrument, analyst, sample type, etc. Therefore, a published MDL may be a useful guide, but is only accurate for a specific set of circumstances. Each analyst should determine a more accurate MDL for each specific sample matrix using the same equipment, reagents and standards that will routinely be used for measurements.

Hach provides a value called the Estimated Detection Limit (EDL) for all programs. It is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. Specifically, it is the upper 99% confidence limit for zero concentration based on the calibration data used to prepare the pre-programmed calibration curve. **Do not use the EDL as the MDL**. The conditions for MDL determination must be exactly the same as the conditions used for analysis. The EDL may be useful to the analyst as a starting point in determining a MDL or as a way to compare methods. Measurements below the EDL may also be valuable because they can show a trend, indicate the presence of analyte and/or provide statistical data. However, these values have a large uncertainty.

Method Detection Limit (MDL)

This method is in accordance with the USEPA definition in 40 CFR, Part 136, Appendix B (see most current edition).

The USEPA defines the method detection limit (MDL) as the minimum concentration that can be determined with 99% confidence that the true concentration is greater than zero. Since the MDL will vary from analyst to analyst, it is important that analysts determine the MDL based on their unique operating conditions.

The procedure for determining MDL is based on replicate analyses at a concentration 1 to 5 times the estimated detection limit. The MDL value is calculated from the standard deviation of the replicate study results multiplied by the appropriate Student's *t* value for a 99% confidence interval. For this definition, the MDL does not account for variation in sample composition and can only be achieved under ideal conditions.

1. Estimate the detection limit. Use the Hach estimated detection limit (EDL) value stated in the *Method Performance* section of the analysis procedure.

2. Prepare a laboratory standard of the analyte in deionized water which is free of the analyte that is 1 to 5 times the estimated detection limit.

3. Analyze at least seven portions of the laboratory standard and record each result.

4. Calculate the average and standard deviation *(s)* of the results.

5. Compute the MDL using the appropriate Student's *t* value (see table below) and the standard deviation value:

MDL = Student's *t* x *s*

Number of Test Portions	Student's *t* Value
7	3.143
8	2.998
9	2.896
10	2.821

For example:
The EDL for measuring iron using the FerroZine method is 0.003 mg/L. An analyst accurately prepared 1 liter of a 0.010 mg/L (about 3x the EDL) laboratory standard by diluting a 10-mg/L iron standard in iron-free deionized water.

Eight portions of the standard were tested according to the FerroZine method with the following results:

Sample #	Result (mg/L)
1	0.009
2	0.010
3	0.009
4	0.010
5	0.008
6	0.011
7	0.010
8	0.009

Using a calculator program, the average concentration = 0.010 mg/L and the standard deviation (*s*) = 0.0009 mg/L

Based on the USEPA's definition, calculate the MDL as follows:

MDL for FerroZine method = 2.998 (Student's *t*) x 0.0009 (*s*)

MDL = 0.003 mg/L (agrees with initial estimate)

Note: *Occasionally, the calculated MDL may be very different than Hach's estimate of the detection limit. To test how reasonable the calculated MDL is, repeat the procedure using a standard near the calculated MDL. The average result calculated for the second MDL derivation should agree with the initial calculated MDL. Refer to 40 CFR, Part 136, Appendix B (7-1-94), pages 635-637 for detailed procedures to verify the MDL determination.*

Note: *Run a laboratory blank, containing deionized water without analyte, through the test procedure to confirm that the blank measurement is less than the calculated MDL. If the blank measurement is near the calculated MDL, repeat the MDL procedure using a separate blank for analysis for each standard solution portion analyzed. Subtract the average blank measurement from each standard and use the corrected standard values to calculate the average and standard deviation used in the MDL.*

Precision

Every measurement has some degree of uncertainty. Just as a ruler with markings of 0.1 mm leaves some doubt as to the exact length of a measurement, chemical measurements also have some degree of uncertainty. The quality of the entire chemical method determines the precision.

Uncertainty in chemical measurements may be due to systematic errors and/or random errors. A systematic error is a mistake that is always the same for every measurement made. For example, a blank can add to each measurement for a specific compound, giving consistently high results (a positive bias). Random errors are different for every test and add either positive or negative bias. Random errors may be caused by variation in analytical technique and cause response variation. Hach chemists work hard to eliminate systematic errors in Hach procedures using Hach reagents, but response variation occurs in all chemical measurements.

Estimating Precision

The method performance section in each procedure provides an estimate of the procedure's precision. The procedures use a "replicate analysis" estimate, based on real data.

In replicate analysis, a Hach chemist prepares a specific concentration of the analyte in a deionized water matrix. The standard is then analyzed seven individual times with the two reagent lots used in the calibration (14 total samples). A standard deviation of the two sets of seven values is calculated. The larger value is reported in the method. The reported value provides an estimate of the "scatter" of results at a particular point in the calibration curve.

It is important to stress that the estimates are based on a deionized water matrix. Precision on real samples with varying matrices can be quite different than these estimates.

Reagent Blank Correction

The Reagent Blank Correction subtracts the color absorbed when running the test with deionized water instead of sample. The blank value is subtracted from every result to correct for any background color due to reagents.

When using the Reagent Blank Correction feature, the blank correction should be entered before the Standard Adjust feature is used.

To enter a programmed correction for the reagent blank:

1. Run the test using deionized water with each new lot of reagents.
2. Press **READ** to obtain the blank value.
3. Press **SETUP**, scroll to **BLANK** and press **ENTER**. The display will show **BLANK?**.
4. Enter the blank value just read from the instrument.
5. Press **ENTER** to accept the value as the blank to be subtracted from each reading.
6. The display will show 0.00 mg/L (resolution and units vary) and the sample cell icon will be displayed, indicating that the reagent blank feature is enabled and the blank value will be subtracted from each reading. Repeat the reagent blank adjust for each new lot of reagents.

Note: *After entering a reagent blank adjust, the display may flash "limit" when zeroing if the sample used for zeroing has a lower absorbance value than the reagent blank.*

To disable the Reagent Blank adjust feature, press **SETUP**, scroll to **BLANK** and press **ENTER** twice. The concentration readings will be displayed without subtracting the blank. The sample cell icon will no longer appear in the display.

Do not use the Reagent Blank Adjust feature if the procedure uses a reagent blank for zeroing.

Standard Adjust (Adjusting the Standard Curve)

The colorimeter has Hach Programs permanently installed in memory. A program usually includes a pre-programmed calibration curve. Each curve is the result of an extensive calibration performed under ideal conditions and is normally adequate for most testing. Deviations from the curve can occur from using compromised testing reagents, defective sample cells, incorrect test procedure, incorrect technique, or other correctable causes. Interfering substances or other causes may be beyond the analyst's control.

In some situations, using the pre-programmed curve may not be convenient:

a) Running tests where frequent calibration curve checks are required.

b) Testing samples which give a consistent test interference.

Consider the following before adjusting the calibration curve:

1. Will future test results be improved by adjusting the curve?
2. Are interfering substances consistent in all the samples that you will test?

Any precision and test range information provided with the procedure may not apply to an adjusted curve calibration.

You can adjust many of the calibration curves by following the steps found in the test procedures. Working carefully is important. After the adjustment, it is wise to run standard solutions of several concentrations to make sure the adjusted curve is satisfactory. Perform standard additions on typical samples to help determine if the adjusted curve is acceptable.

Think of the standard adjust measurement as a two-step process. First, the instrument measures the sample using the pre-programmed calibration. Second, it multiplies this measurement by an adjustment factor. The factor is the same for all concentrations. The instrument will remember the factor indefinitely and will display the standard adjustment icon when it is used.

Adjust the calibration curve using the reading obtained with a Hach Standard Solution or carefully prepared standard made from a concentrated Hach Standard Solution. It is important to adjust the curve in the correct concentration range. For most purposes, Hach recommends adjusting the curve using a standard concentration that is 70 to 85% of the maximum concentration range of the test.

For example, the Hach pre-programmed method for fluoride has a range of 0-2.0 mg/L F. To adjust the calibration curve, use a standard with a concentration between 1.4-1.6 mg/L. Hach provides a 1.60 mg/L Fluoride Standard Solution (80% of the full range). This is a convenient standard to use for adjusting the calibration curve.

If the range of all your samples is known to be below a concentration that is less than 50% of the full range (50% of 2.0 is 1.0 mg/L), then adjust the standard curve with a standard that is within that range. For example, if all the samples contain 0.6-0.9 mg/L F, you may use a 1.00 mg/L fluoride standard to adjust the curve. You may use the 1.00 mg/L standard because it is closer to the sample range you are working with.

If you are using a Reagent Blank Correction, the blank correction should be entered before the standard curve is adjusted.

To adjust the standard curve:

1. Prepare the standard.
2. Use the standard as the sample in the procedure.
3. When the reading for the standard is obtained, press **SETUP**.
4. Use the arrow keys to scroll to the "**STD**" setup option.
5. Press **ENTER** to activate the standard adjust option.
6. Edit the standard concentration to match that of the standard used.
7. Press **ENTER**. A small plot of a line through a point will be displayed, indicating that the curve has been adjusted with the standard.

Note: *If the attempted correction is outside the allowable adjustment limit, the instrument will beep and flash Ø and the operation will not be allowed.*

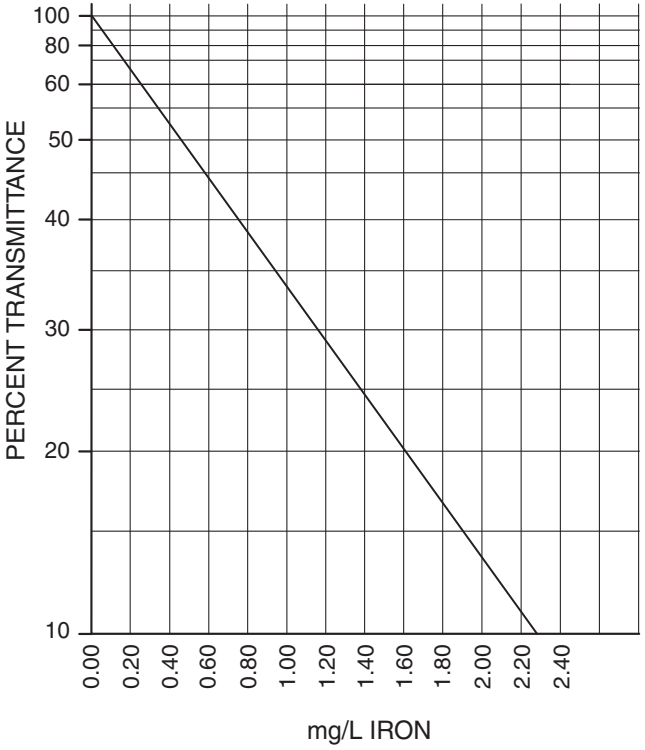
Preparing a User-Entered Calibration Curve

1. Prepare five or more standards of known concentration that cover the expected range of the test. Run tests as described in the procedure on each prepared standard. Pour the customary volume of each known solution into a separate clean sample cell of the type specified for your instrument.
2. Standardize (zero) the instrument using an untreated water sample or a reagent blank, whichever the procedure instructs you to use.
3. Measure and record the absorbance or %T of the known solutions. To use %T vs. concentration see *%T Versus Concentration Calibration*. To use absorbance vs. concentration, see *Absorbance Versus Concentration Calibration*. Or create a user-entered program by storing a custom calibration in the non-volatile memory of the instrument. Refer to the section on entering user-entered programs in the instrument manual.

%T Versus Concentration Calibration

If measuring %T, use semilogarithmic graph paper and plot %T (vertical scale) versus concentration (horizontal scale). In *Figure 11*, iron standard solutions of 0.1, 0.2, 0.4, 0.8, 1.2, 1.6, and 2.0 mg/L were measured on a spectrophotometer at 500 nm using half-inch test tubes. Results were plotted and the calibration table values were extrapolated from the curve (*Table 7*).

Figure 11 Logarithmic Calibration Curve



To convert %T readings to concentration, prepare a table such as *Table 7* and select the appropriate line from the "%T Tens" column and the appropriate column from the %T Units columns. The %T Ten value is the first number of the %T reading and the %T Units value is the second number of the %T reading. For example, if the instrument reading was 46%, the 40 line in the %T Tens column and the 6 column in the %T Units would be selected. The cell where these two intersect (0.78 mg/L) is the iron concentration of the sample.

Table 7 Calibration Table

%T Tens	%T Units									
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
0										
10	2.30	2.21	2.12	2.04	1.97	1.90	1.83	1.77	1.72	1.66
20	1.61	1.56	1.51	1.47	1.43	1.39	1.35	1.31	1.27	1.24
30	1.20	1.17	1.14	1.11	1.08	1.04	1.02	.99	.97	.94
40	.92	.89	.87	.84	.82.	.80	.78	.76	.73	.71
50	.69	.67	.65	.64	.62	.60	.58	.56	.55	.53
60	.51	.49	.48	.46	.45	.43	.42	.40	.39	.37
70	.36	.34	.33	.32	.30	.29	.28	.26	.25	.24
80	.22	.21	.20	.19	.17	.16	.15	.14	.13	.12
90	.11	.09	.08	.07	.06	.05	.04	.03	.02	.01

Absorbance Versus Concentration Calibration

To read concentration values directly from the instrument, create a user-entered program. See the instrument manual for more information.

If absorbance values are measured, plot the results on linear graph paper. Plot the absorbance value on the vertical axis and the concentration on the horizontal axis.

Plot increasing absorbance values from bottom to top. Plot increasing concentration values from left to right. Values of 0.000 absorbance units and 0 concentration will begin at the bottom left corner of the graph. A calibration table can be extrapolated from the curve or the concentration values can be read directly from the graph for determining an equation for the line using the slope and the y-intercept.

USEPA Approved and Accepted Definitions

The United States Environmental Protection Agency (USEPA) establishes limits for maximum contamination levels of certain constituents in water. It also requires that specific methodology be used to analyze for these constituents. These methods originate from several sources. The USEPA has developed some of these methods. In other cases, the USEPA has evaluated and approved methods developed by manufacturers, professional groups and public agencies such as:

- American Public Health Association

- American Water Works Association
- Water Environmental Federation
- American Society for Testing and Materials
- United States Geological Survey
- Associates of Official Analytical Chemists

All USEPA approved methods are cited in the *Federal Register* and compiled in the Code of Federal Regulations. USEPA approved methods may be used for reporting results to the USEPA and other regulatory agencies.

USEPA Accepted

Hach has developed several procedures that are equivalent to USEPA approved methods. Even though minor modifications exist, the USEPA has reviewed and accepted certain procedures for reporting purposes. These methods are not published in the *Federal Register,* but are referenced to the equivalent USEPA method in the procedure.

Digestion

Several procedures require sample digestion. Digestion uses chemicals and heat to break down a substance into components that can be analyzed. This section has three different digestion procedures.

The Hach Digesdahl® system is a process that yields a digest suitable for the determination of metals, total phosphorus and total kjeldahl nitrogen (TKN). It is rapid, convenient and the method of choice for digesting most samples analyzed by Hach methods.

For USEPA reporting purposes, USEPA-approved digestions are required. USEPA presents two digestions (mild and vigorous) for metals analysis. These are much more inconvenient and time consuming compared to the Hach Digesdahl system. Other digestion procedures are required for phosphorus and TKN.

EPA Mild Digestion with Hot Plate for Metals Analysis Only

1. Acidify the entire sample at the time of collection with concentrated nitric acid by adding 5 mL of acid per liter (or quart) of sample.

2. Transfer 100 mL of well-mixed sample to a beaker or flask. Add 5 mL of distilled 1:1 hydrochloric acid (HCl).

3. Heat using a steam bath or hot plate until the volume has been reduced to 15-20 mL. Make certain the sample does not boil.

4. After this treatment, the sample may be filtered to remove any insoluble material.

5. Adjust the digested sample to pH 4 by drop-wise addition of 5.0 N Sodium Hydroxide Standard Solution. Mix thoroughly and check the pH after each addition.

6. Quantitatively transfer the sample with deionized water to a 100-mL volumetric flask and dilute to volume with deionized water. Continue with the procedure. This mild digestion may not suffice for all sample types. A reagent blank also should be carried through the digestion and measurement procedures.

EPA Vigorous Digestion with Hot Plate for Metals Analysis Only

A vigorous digestion can be followed to ensure all organo-metallic bonds are broken.

1. Acidify the entire sample with redistilled 1:1 Nitric Acid Solution to a pH of less than two. Do not filter the sample before digestion.

2. Transfer an appropriate sample volume (see *Table 8*) into a beaker and add 3 mL of concentrated redistilled nitric acid.

3. Place the beaker on a hot plate and evaporate to near dryness, making certain the sample does not boil.

4. Cool the beaker and add another 3 mL of the concentrated redistilled nitric acid.

5. Cover the beaker with a watch glass and return it to the hot plate. Increase the temperature of the hot plate so that a gentle reflux occurs. Add additional acid, if necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change color or appearance with continued refluxing).

6. Again, evaporate to near dryness (do not bake) and cool the beaker. If any residue or precipitate results from the evaporation, add redistilled 1:1 hydrochloric acid (5 mL per 100 mL of final volume). See *Table 8*.

7. Warm the beaker. Add 5 mL of 5.0 N sodium hydroxide and quantitatively transfer the sample with deionized water to a volumetric flask. See *Table 8* below for the suggested final volume.

8. Adjust the sample to pH 4 by drop-wise addition of 5.0 N Sodium Hydroxide Standard Solution; mix thoroughly and check the pH after each addition. Dilute to volume with deionized water. Multiply the result by the correction factor in *Table 8*. A reagent blank also should be carried through the digestion and measurement procedures.

Table 8 Vigorous Digestion Volumes

Expected Metal Concentration	Suggested Sample Vol. for Digestion	Suggested Volume of 1:1 HCl	Suggested Final Volume After Digestion	Correction Factor
1 mg/L	50 mL	10 mL	200 mL	4
10 mg/L	5 mL	10 mL	200 mL	40
100 mg/L	1 mL	25 mL	500 mL	500

General Digesdahl Digestion (Not USEPA accepted)

Many samples may be digested using the Digesdahl Digestion Apparatus (Cat. No. 23130). It is designed to digest many types of samples such as oils, wastewater, sludges, feeds, grains, plating baths, food, and soils. In this procedure the sample is oxidized by a mixture of sulfuric acid and hydrogen peroxide. Digestion of a dry sample requires less than ten minutes, while liquid samples require about 1 minute/mL. The digestion is done in a special flat-bottomed 100-mL volumetric flask. Aliquots (sample portions) are taken for analysis using colorimetric methods.

Procedures for digestion and using the Digesdahl Digestion Apparatus are based on the type and form of the sample, and are found in the Digesdahl Digestion Apparatus Instruction Manual, which is included with each Digesdahl Digestion Apparatus.

Distillation

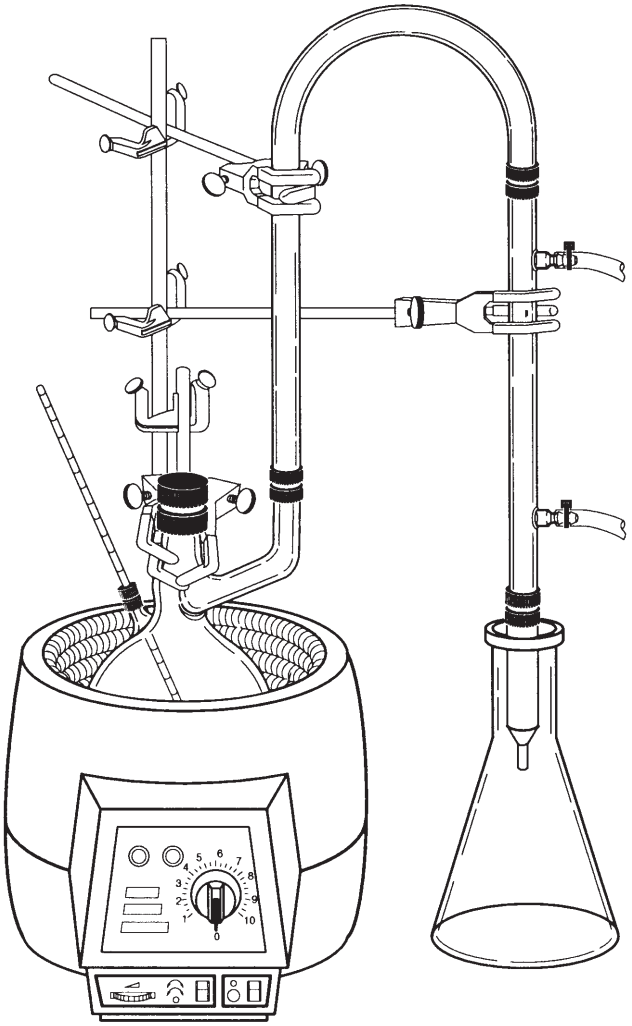
Distillation is an effective way of separating chemical components for analysis. The Hach Distillation Apparatus (see *Figure 12*) is adapted easily for many test needs and is suitable for water and wastewater samples. Sample distillations are easy and safe to perform.

Applications for the General Purpose Distillation Apparatus include:

- fluoride
- albuminoid nitrogen
- ammonia nitrogen
- phenols
- selenium
- volatile acids

Arsenic and cyanide require special glassware sets in addition to the General Purpose Set (the Arsenic Distillation Apparatus and the Cyanide Distillation Apparatus). All connecting glassware is manufactured with threaded connectors for ease and safety. The General Purpose Heater provides efficient heating and the Support Apparatus anchors the glassware.

Figure 12 General Purpose Distillation Apparatus with Heater and Support Apparatus



SECTION 3 WASTE MANAGEMENT AND SAFETY

Waste Management

This section provides guidelines for laboratory waste management. It should assist you in complying with USEPA regulations governing waste management. It summarizes basic requirements, but does not contain all USEPA regulations. It does not relieve people from complying with all regulations contained in the Code of Federal Regulations. Regulations change regularly and additional state and local laws may apply to your waste. Each waste generator is responsible for knowing and obeying the laws that apply to them.

Waste Minimization

Waste minimization is the foundation of good waste management. Minimizing waste greatly reduces the disposal problems and expense. If possible, try to generate less waste rather than recycle or re-use it. For laboratories, ways to reduce waste include:

- Use the smallest sample size possible.
- Choose methods that use non-hazardous or “less” hazardous reagents when possible.
- Buy chemicals in small quantities which will be used before they expire. This eliminates disposal of outdated materials.
- Clean glassware and laboratory apparatus with non-hazardous soaps when possible, rather than solvents or acids which may be hazardous.

Regulatory Overview

Federal waste disposal regulations were issued in accordance with the Resource Conservation and Recovery Act (RCRA). They are given in Title 40 Code of Federal Regulations (CFR) part 260. The Act controls all forms of solid waste disposal and encourages recycling and alternative energy sources. The major emphasis is controlling hazardous waste disposal. The regulations create a system to identify wastes and track waste generation, transport, and ultimate disposal. Each facility involved in managing hazardous waste must be registered with the USEPA. This includes the generator, transporters, and treatment, storage, and disposal facilities (TSDF).

Under federal regulations, there are three categories of generators with increasingly more strict regulation for larger quantity generators. The categories are based on the amount of hazardous waste generated in any given month.

The categories are as follows:

- Conditionally Exempt Small Quantity Generator - less than 100 kg (220 lb.) per month
- Small Quantity Generator - between 100 kg (220 lb.) and 1,000 kg (2,200 lb.) per month
- Large Quantity Generator - greater than 1,000 kg (2,200 lb.) per month

Note: *If a laboratory generates acutely hazardous waste (as defined on 40 CFR 261) or accumulates more than a certain amount of waste, the facility may be moved into a larger generator status. Check with your environmental compliance manager or state and local officials to determine which category your facility is in.*

Hazardous Waste Definition

For regulatory purposes, a "hazardous waste" is a material which is subject to special laws by the USEPA under 40 CFR 261. In addition, many states or local authorities regulate additional materials as hazardous waste. Be aware that many very toxic compounds are not regulated by this definition of hazardous waste. However, improper management or disposal of these compounds may lead to legal problems under other laws such as CERCLA (Superfund) or common law torts.

The 40 CFR 261 defines a hazardous waste as a solid waste which is not excluded from regulation and meets any of the following criteria:

- It is a discarded commercial chemical product, off-specification species, container residue, or spill residue of materials specifically listed in 40 CFR 261.33;
- It is a waste from a specific source listed in 40 CFR 261.32;
- It is a waste from a non-specific source listed in 40 CFR 261.31; or
- It displays any of the following characteristics of hazardous waste defined in 40 CFR 261.20-24:
    - ignitability
    - corrosivity
    - reactivity
    - toxicity

There are many exceptions to these regulations, and each generator should review the regulations and determine if they are excluded from the regulations.

Characteristic Hazardous Waste Codes

Hazardous wastes are categorized by specific codes assigned in 40 CFR 261.20-261.33. These codes will help you identify hazardous waste. The generator is responsible for making the actual waste code determination.

Selected characteristic waste codes for chemicals which may be generated using Hach methods for water analysis are given in the following table. A complete list of waste codes is found in 40 CFR 261.24.

USEPA Code	Characteristic	CAS No.	Regulatory Level (mg/L)
D001	Ignitability	na	na
D002	Corrosivity	na	na
D003	Reactivity	na	na
D004	Arsenic	6440-38-2	5.0
D005	Barium	6440-39-3	100.0
D018	Benzene	71-43-2	0.5
D006	Cadmium	7440-43-9	1.0
D022	Chloroform	67-66-3	6.0
D007	Chromium	7440-47-3	5.0
D008	Lead	7439-92-1	5.0
D009	Mercury	7439-97-6	0.2
D010	Selenium	7782-49-2	1.0
D011	Silver	7440-22-4	5.0

How to Determine if Waste is Hazardous

Federal laws do not require you to test a material to decide if it is a hazardous waste. You may apply product knowledge to decide if a material is hazardous. Often, information on a material safety data sheet (MSDS) is enough to decide. If the product is specifically listed in the regulation, it is a hazardous waste.

You also need to decide if it has any characteristics of a hazardous waste. Physical information on the MSDS may help you decide. If the flash point is below 60 °F (15 °C) or is classified by DOT as an oxidizer, the material may be ignitable. If the pH of the material is ≤2 or ≥12.5, the material may be corrosive. If the material is unstable, reacts violently with water, or may generate toxic gases, vapors, or fumes when mixed with water, it may be reactive.

Use the chemical composition data to decide if a material is toxic. This decision is based on the concentration of certain contaminants (heavy metals and a number of organic compounds). If the waste is a liquid, compare the concentration of the contaminants in the liquid to the concentrations listed in 40 CFR 261.24. If the waste is a solid, analyze the sample by the Toxicity Characteristic Leachability Procedure (TCLP) and compare the results to the concentration listed in the 40 CFR 261.24. Levels above the threshold amount listed in the table are hazardous.

See "Sections of the MSDS" on page 63. describing the MSDS for help in finding information for making hazardous waste determinations.

Examples of Hazardous Waste

A number of chemicals used in and final solutions created from Hach procedures are hazardous wastes when they are disposed. In addition, substances in the sample matrix may be a hazardous waste. Sometimes, reagents which would be hazardous are neutralized or changed during the analytical procedure. In that case, the final solutions are not regulated. Finally, many reagents and final solutions may be non-regulated. The generator must either use their knowledge of the materials used or conduct analytical tests to determine if the final material is a hazardous waste.

Examples of tests using Hach reagents that generate hazardous waste include those containing mercury or mercury compounds such as COD tests or Nessler's reagent. Conversely, a test using Hach reagents such as ManVer 2 Hardness Indicator Powder Pillows and EDTA Titration Cartridges do not produce a hazardous waste unless the sample contains a hazardous substance.

Hazardous Waste Disposal

Hazardous waste must be managed and disposed of according to federal, state, and local regulations. The waste generator is responsible for making hazardous waste determinations. Analysts should check with the facility's environmental compliance people for specific instructions.

Hazardous wastes should be handled by treatment, storage, and disposal facilities (TSDF) that have USEPA permits. In some cases, the generator may treat the hazardous waste. In most cases, a permit from the USEPA is required to treat hazardous waste. Laboratories are not exempt from these regulations. If your facility is a "Conditionally Exempt Small Quantity Generator," special rules may apply. Check 40 CFR 261 to determine if have to comply with all the laws.

The most common allowed treatment is elementary neutralization. This refers to neutralizing wastes that are hazardous only because they are corrosive or are listed only for that reason. Neutralize acidic solutions by adding a base such as sodium hydroxide; neutralize basic solutions by

adding an acid such as hydrochloric acid. Slowly add the neutralizing agent while stirring. Monitor the pH. When it is at or near 7, the material is neutralized and may be flushed down the drain. Many wastes generated from Hach procedures may be treated in this manner.

Other chemical or physical treatments such as cyanide destruction or evaporation may require a permit. Check with your environmental department or local regulators to determine which rules apply to your work facility.

Laboratory chemicals may be mixed and disposed of with other hazardous wastes generated at your facility. They may also be accumulated in accordance with 40 CFR 262.34 satellite accumulation rules. After collection they may be disposed of in a "labpack." A number of environmental and hazardous waste companies offer labpacking services. They will inventory, sort, pack, and arrange proper disposal for hazardous waste. Find companies offering these services in the Yellow Pages under "Waste Disposal - Hazardous" or contact state and local regulators for assistance.

Management of Specific Wastes

Hach has several documents to assist customers in managing waste generated from our products. You can obtain the following documents by calling 1-800-227-4224 or 970-669-3050 and requesting the literature codes given:

Literature Code	Title
1321	Waste Reduction: A Primer
9323	Mercury Waste Disposal Firms
9325	COD Waste Management
9326	COD Heavy Metal Total Concentrations

Special Considerations for Cyanide-Containing Materials

Several procedures in this manual use reagents that contain cyanide compounds. These materials are regulated as reactive (D003) waste by the Federal RCRA. Waste disposal instructions provided with each procedure tell you how to collect these materials for proper disposal. It is imperative that these materials be handled safely to prevent the release of hydrogen cyanide gas (an extremely toxic material with the smell of bitter almonds). Most cyanide compounds are stable and can be safely stored for disposal in highly alkaline solutions (pH >11) such as 2 N sodium hydroxide. Never mix these wastes with other laboratory wastes that may contain lower pH materials such as acids or even water.

If a cyanide-containing compound is spilled, you must be careful not to be exposed to hydrogen cyanide gas. Take the following steps to destroy the cyanide compounds in an emergency:

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

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

c) Add an excess of hydroxide and hypochlorite. Let the solution stand for 24 hours.

d) Neutralize the solution and flush it down the drain with a large amount of water. If the solution contains other regulated materials such as chloroform or heavy metals, it may still need to be collected for hazardous waste disposal. Never flush hazardous wastes down the drain.

Resources

Many sources of information on proper waste management are available. The USEPA has a hotline number for questions about the Resource Conservation and Recovery Act (RCRA). The RCRA Hotline number is 1-800-424-9346. You may also get a copy of the appropriate regulations. Federal hazardous waste regulations are found in 40 CFR 260- 99. Obtain this book from the U.S. Government Printing Office or a number of other vendors. Other documents which may be helpful to the laboratory hazardous waste manager include:

1. Task Force on Laboratory Waste Management. *Laboratory Waste Management, A Guidebook*; American Chemical Society, Department of Government Relations and Science Policy: Washington, DC 1994.

2. Task Force on Laboratory Waste Management. *Waste Management Manual for Laboratory Personnel*; American Chemical Society, Department of Government Relations and Science Policy: Washington, DC 1990.

3. Task Force on Laboratory Waste Management. *Less is Better*; 2nd ed.; American Chemical Society, Department of Government Relations and Science Policy: Washington, DC 1993.

4. Committee on Chemical Safety. *Safety in Academic Chemistry Laboratories*, 5th ed.; American Chemical Society: Washington, DC, 1990.

5. Armour, Margaret-Ann. *Hazardous Laboratory Chemicals Disposal Guide*; CRC Press: Boca Raton, FL, 1991.

6. *Environmental Health and Safety Manager's Handbook*; Government Institutes, Inc.: Rockville, MD, 1988.

7. Lunn, G.; Sansone, E.B. *Destruction of Hazardous Chemicals in the Laboratory*; John Wiley and Sons: New York, 1990.

8. National Research Council. *Prudent Practices for Disposal of Chemicals from Laboratories*; National Academy Press: Washington, DC, 1983.

9. National Research Council. *Prudent Practices for Handling Hazardous Chemicals in Laboratories*; National Academy Press: Washington, DC, 1981.

10. Environmental Protection Agency, Office of Solid Waste and Emergency Response. *The RCRA Orientation Manual*; U.S. Government Printing Office: Washington, DC, 1991.

11. Environmental Protection Agency, Office of Solid Waste and Emergency Response. *Understanding the Small Quantity Generator Hazardous Waste Rules: A Handbook for Small Business*; U.S. Government Printing Office: Washington, DC, 1986.

Material Safety Data Sheets

Material safety data sheets (MSDS) describe the hazards of chemical products. This section describes the information provided on a Hach MSDS and how to locate important information for safety and waste disposal. The information provided on the MSDS applies to the product as sold by Hach. The properties of any mixtures obtained by using this product will be different.

How to Obtain an MSDS

Hach ships an MSDS to each customer with the first order of any chemical product. A new MSDS may be sent when the information on the data sheet is updated. Please review all new MSDS's for new information. If you need another copy of an MSDS, simply call 1-800-227-4227.

Sections of the MSDS

Each MSDS has ten sections. The sections and the information found in them are described below.

Header Information

The Hach catalog number, MSDS date, change number, company address and telephone number, and emergency telephone numbers are listed at the top of the MSDS.

1 Product Identification

This section contains:

- Hach product name
- Chemical Abstract Services (CAS) number
- Chemical name
- Chemical formula, if appropriate
- Chemical family to which the material belongs

2 Ingredients

This section lists each component in the product. It contains the following information for each component:

- PCT: Percent by weight of this component
- CAS NO.: Chemical Abstract Services (CAS) registry number for this component
- SARA: Superfund Amendments and Reauthorization Act, better known as the "Community Right to Know Law" tells you if the component is listed in SARA 313. If the component is listed and you use more than the amount listed, you must report this to the USEPA every year.
- TLV: Threshold Limit Value. The maximum airborne concentration for an 8 hour exposure that is recommended by the American Conference of Governmental Industrial Hygienists (ACGIH).
- PEL: Permissible Exposure Limit. The maximum airborne concentration for an 8 hour exposure that is regulated by the Occupational Safety and Health Administration (OSHA).
- HAZARD: Physical and health hazards of the component are explained.

3 Physical Data

The physical properties of the product are given in this section. They include the physical state, color, odor, solubility, boiling point, melting point, specific gravity, pH, vapor density, evaporation rate, corrosivity, stability, and storage precautions.

4 Fire, Explosion Hazard And Reactivity Data

This section contains the flash point and flammable limits of the material. It also includes how to fight fires if the material catches on fire. Key terms in this section include:

- Flashpoint: The temperature at which a liquid will give off enough flammable vapor to ignite.
- Flammability and ignitability are usually defined by the flash point.
- Lower Flammable Limit (LFL or LEL): The lowest concentration that will produce a fire or flash when an ignition source is present.
- Upper Flammable Limit (UFL or UEL): The vapor concentration in air above which the concentration is too rich to burn.
- NFPA Codes: The National Fire Protection Association (NFPA) has a system to rate the degree of hazards presented by a chemical. These codes are usually placed in a colored diamond. The codes range from 0 for minimal hazard to 4 for extreme hazard. They are grouped into the following hazards: health (blue), flammability (red), reactivity (yellow), and special hazards (white).

5 Health Hazard Data

This section describes different ways the chemical can enter your body (ingestion, inhalation, skin contact). It also gives acute (immediate) and chronic (long-term) health effects. If the material causes cancer or genetic damage, it is identified in this section.

6 Precautionary Measures

This section contains special precautions for the material. These may include special storage instructions, handling instructions, conditions to avoid, and protective equipment required to use this material safely.

7 First Aid

First aid instructions for exposures to the chemical are given in this section. Be sure to read this section before inducing vomiting in a victim. Some chemicals are better treated by not inducing vomiting. Seek prompt medical attention for all chemical exposures.

8 Spill And Disposal Procedures

This section tells about safe work practices for cleaning up and disposing of spilled material. Please refer to the Waste Management section of this manual. Final determination of proper and legal disposal options is the responsibility of the waste generator. Be sure you know the federal, state, and local laws that apply to your facility.

9 Transportation Data

Domestic and International shipping information is provided in this section. It gives shipping name, hazard class, and ID number of the product.

10 References

This section lists the reference materials used to write the MSDS.

Following the Reference section, the product is listed as having SARA 313 chemicals or California Proposition 65 List Chemicals, if applicable. Also found here is any special information about the product.

Safety

Safety is the responsibility of each person performing analytical procedures. Because many of the procedures in this methods manual use potentially hazardous chemicals and equipment, it is important to prevent accidents by practicing good laboratory techniques. The following guidelines apply to water analysis. These guidelines do not cover every aspect of safety, but they are important for preventing injuries.

Material Safety Data Sheet

A material safety data sheet (MSDS) comes with the first shipment of all products. The MSDS provides environmental and safety information about the products. Always read the MSDS before using a new product.

Reading Labels Carefully

Read each reagent label carefully. Pay particular attention to the precautions given. Never remove or block the label on a reagent container while it contains reagent. Do not put a different reagent into a labeled container without changing the label. When preparing a reagent or standard solution, label the container clearly. If a label is hard to read, re-label promptly according to your facility's hazard communication program.

Warning labels also appear on some of the apparatus used with the test procedures. The protective shields with the COD Reactor and the Digesdahl Digestion Apparatus point out potential hazards. Be sure these shields are in place during use and observe the precautions on the label.

Protective Equipment

Use the right protective equipment for the chemicals and procedures. The MSDS contains this information. Protective equipment may include:

- Eye protection such as safety glasses or goggles to protect from flying objects or chemical splashes.
- Gloves to protect skin from toxic or corrosive materials, sharp objects, very hot or very cold materials, or broken glass. Use tongs or finger cots when transferring hot apparatus.

- Laboratory coats or splash aprons to protect skin and clothing from splashes.
- Footwear to protect feet from spills. Open toed shoes should not be worn in chemistry settings.
- Respirators may be needed to protect you from breathing toxic vapors if adequate ventilation, such as fume hoods, are not available.
- Use fume hoods as directed by the procedure or as recommended in the MSDS.
- For many procedures, adequate ventilation is enough. Be sure there is enough fresh air and air exhaust to protect against unnecessary exposure to chemicals.

First Aid Equipment and Supplies

Most first aid instructions for chemical splashes in eyes or on skin call for thorough flushing with water. Laboratories should have eyewash and shower stations. For field work, carry a portable eyewash unit. Laboratories should also have appropriate fire extinguishers and fume hoods.

General Safety Rules

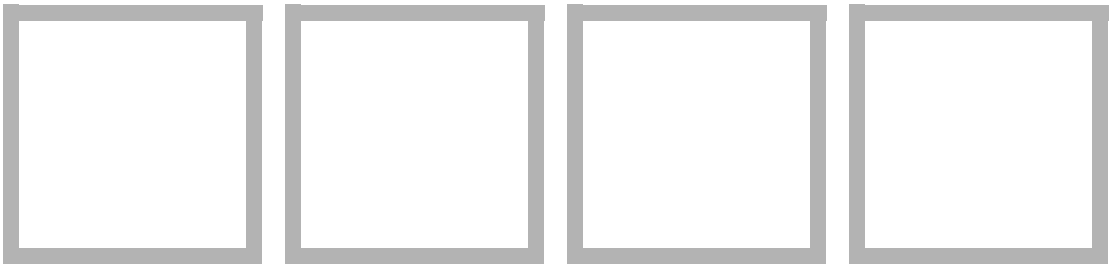
Follow these rules to make work with toxic and hazardous chemicals safer:

1. **Never** pipet by mouth. Always use a mechanical pipet or pipet bulb to avoid ingesting chemicals.
2. Follow test procedures carefully and observe all precautionary measures. Read the entire procedure carefully before beginning.
3. Wipe up all spills promptly. Get proper training and have the right response equipment to clean up spills. See your safety director for more information.
4. **Do not** smoke, eat, or drink in an area where toxic or irritating chemicals are used.
5. Use reagents and equipment only as directed in the test procedure.
6. **Do not** use damaged labware and broken equipment.
7. Minimize all chemical exposures. **Do not** breathe vapors or let chemicals touch your skin. Wash your hands after using chemicals.
8. Keep work areas **neat** and **clean**.

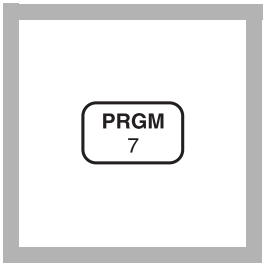
9. **Do not** block exits or emergency equipment.

OSHA Chemical Hygiene Plan

The Occupational Safety and Health Administration (OSHA) enforces laws about the control exposure to hazardous chemicals in laboratories. These regulations are in Title 29 CFR 1910.1450. They apply to all employers who use hazardous chemicals. They require employers to develop and use a written Chemical Hygiene Plan and appoint a qualified person as the Chemical Hygiene Officer.



Aluminon Method*



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

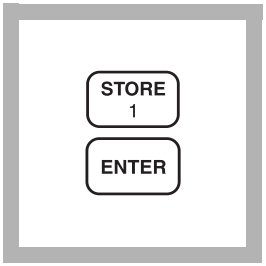
Press: **PRGM**

The display will show:

PRGM ?

Note: *Adjust the pH of stored samples before analysis.*

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

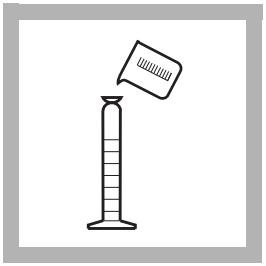


2. Press: **1 ENTER**

The display will show **mg/L, Al** and the **ZERO** icon**.**

Note: *Total aluminum determination requires a digestion prior to analysis (see Section 2).*

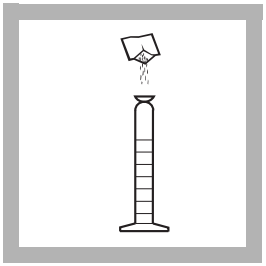
Note: *For alternate form (Al_2O_3), press* **CONC**.



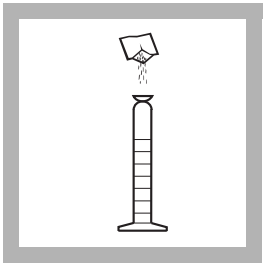
3. Fill a 50-mL graduated mixing cylinder to the 50-mL mark with sample.

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

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



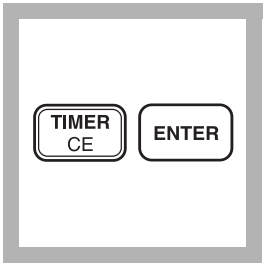
4. Add the contents of one Ascorbic Acid Powder Pillow. Stopper. Invert several times to dissolve powder.



5. Add the contents of one AluVer® 3 Aluminum Reagent Powder Pillow. Stopper.

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

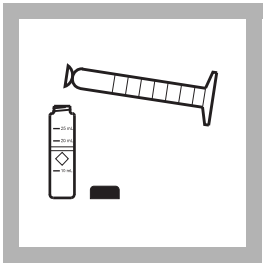
Note: *Inconsistent results will occur if any powder is undissolved.*



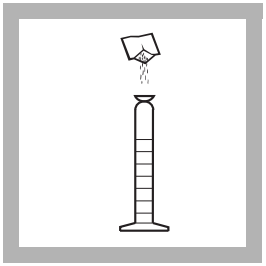
6. Press:

TIMER ENTER

A three-minute reaction period will begin. Invert the cylinder repeatedly for the three minutes.

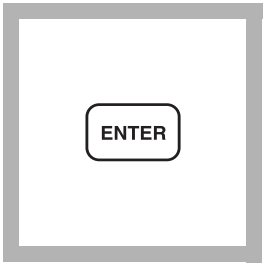


7. Pour 25 mL of mixture into a 25-mL sample cell (the prepared sample).



8. Add the contents of one Bleaching 3 Reagent Powder Pillow to the remaining 25 mL in the mixing graduated cylinder (the blank). Stopper the cylinder.

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

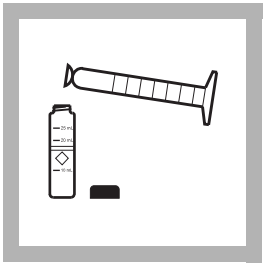


9. The display will show: **00:30 Timer 2**

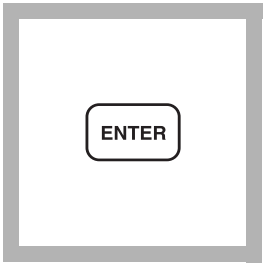
Press: **ENTER**

A thirty-second reaction period will begin. Vigorously shake the cylinder for the 30-second period.

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



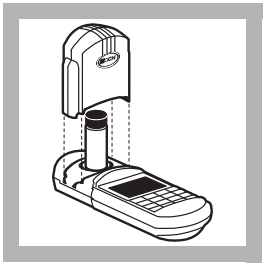
10. Pour the 25 mL of mixture in the cylinder into a second 25-mL sample cell (the blank).



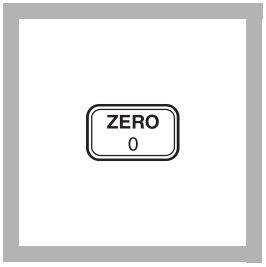
11. The display will show: **15:00 TIMER 3**

Press: **ENTER**

A 15-minute reaction period will begin.



12. Within three minutes after the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

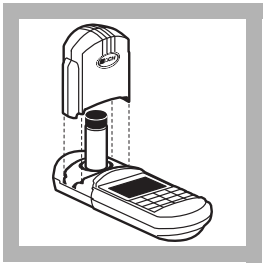


13. Press: **ZERO**

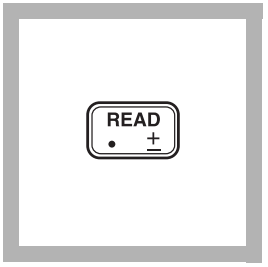
The cursor will move to the right, then the display will show:

0.000 mg/L Al

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



14. Immediately place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



15. Press: **READ**

The cursor will move to the right, 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: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in a clean 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 3.5–4.5 with 5.0 N Sodium Hydroxide. Correct the test result for volume additions; see *Correcting for Volume Additions* in *Section 1* for more information.

Accuracy Check

Standard Additions Method

a) Snap the neck off an Aluminum Voluette Ampule Standard Solution, 50 mg/L as 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. Swirl gently to mix. Also prepare a sample without any standard added (the unspiked sample).

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 (Section 1)* for more information.

Standard Solution Method

Prepare a 0.40-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 deionized water. Prepare this solution immediately before use. Perform the aluminum procedure as described above. The mg/L Al reading should be 0.40 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 deionized water. Prepare this standard immediately before testing and use as the sample.

Method Performance

Precision

In a single laboratory, using a standard solution of 0.40 mg/L Al and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.013 mg/L Al.

Estimated Detection Limit

The estimated detection limit for program #1 is 0.013 mg/L Al. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Acidity	Acidity interferes at greater than 300 mg/L as $CaCO_3$. Treat samples with greater than 300 mg/L acidity as $CaCO_3$ as follows: **1.** Add one drop of m-Nitrophenol Indicator Solution to the sample taken in Step 3. **2.** 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. **3.** Add one drop of 5.25 N Sulfuric Acid Standard Solution to change the solution from yellow back to colorless. Continue with the test.
Alkalinity	1000 mg/L as $CaCO_3$. Eliminate interferences from higher alkalinity concentrations using the following pretreatment: **1.** Add one drop of m-Nitrophenol Indicator Solution to the sample taken in Step 3. A yellow color indicates excessive alkalinity. **2.** 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 becomes colorless. Continue with the test.
Calcium	Does not interfere.
Fluoride	Interferes at all levels. See graph below.
Iron	Greater than 20 mg/L.
Phosphate	Greater than 50 mg/L.
Polyphosphate	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 procedures.

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:

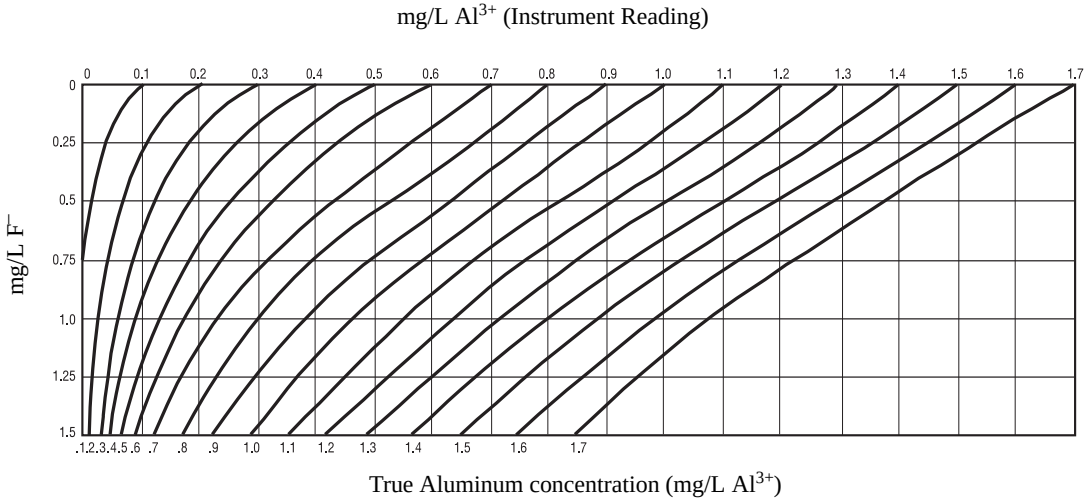
1. Select the vertical grid line along the top of the graph that represents the aluminum reading obtained in Step 15.

2. Locate the point of the vertical line (instrument reading) where it intersects with the horizontal grid line that indicates how much fluoride is present in the sample.

3. 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^{3+} and the fluoride present in the sample was 1.0 mg/L F^-, the point where the 0.7 grid line intersects with the 1.0 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.

Fluoride Interference Graph



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: (1) 14290-99, (1) 14577-99, (1) 14294-49	

Description	Quantity Required Per Test	Unit	Cat. No.
AluVer 3 Aluminum Reagent Powder Pillow	1 pillow	100/pkg	14290-99
Ascorbic Acid Powder Pillow	1 pillow	100/pkg	14577-99
Bleaching 3 Reagent Powder Pillow	1 pillow	100/pkg	14294-49

REQUIRED APPARATUS

Cylinders, graduated mixing, 50 mL	1	each	1896-41
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

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
Hydrochloric Acid Solution, 6N (1:1)	500 mL	884-49
m-Nitrophenol Indicator Solution, 10 g/L	100 mL	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	50 mL SCDB	2450-26
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Brush	each	690-00
Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, volumetric, Class A, 250 mL	each	14574-46
Fluoride Combination Electrode	each	51928-00
Fluoride ISA Powder Pillows	25/pkg	2589-99
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH/ISE Meter, *sens**ion**™2*, portable	each	51725-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Pipet, Volumetric, Class A, 1.00 mL	each	14515-35
Thermometer, –20 to 110 °C, non-mercury	each	26357-02

For Technical Assistance, Price and Ordering

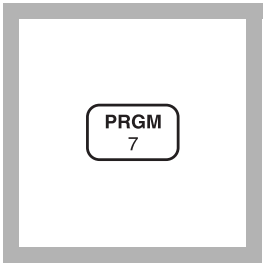
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

BROMINE (0 to 4.50 mg/L)

DPD Method* (Powder Pillows or AccuVac Ampuls)

Using Powder Pillows



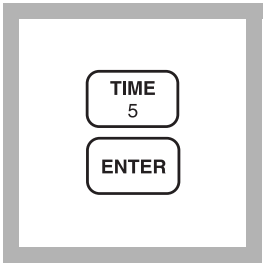
1. Enter the stored program number for bromine (Br_2)-powder pillows.

Press: **PRGM**

The display will show:

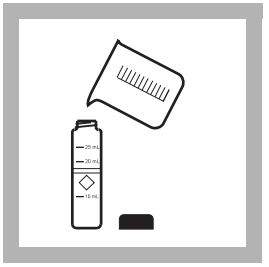
PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



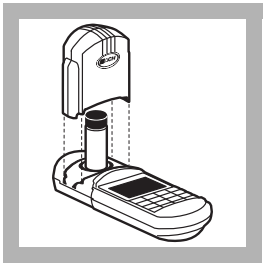
2. Press: **5 ENTER**

The display will show **mg/L, Br2** and the **ZERO** icon**.**



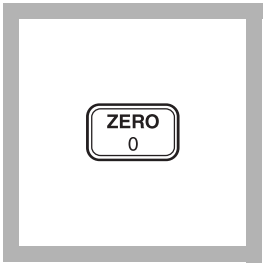
3. Fill a sample cell with 10 mL of sample (the blank).

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



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

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

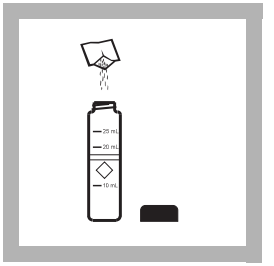


5. Press: **ZERO**

The cursor will move to the right, then the display will show:

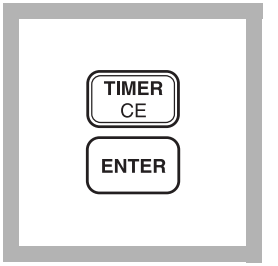
0.00 mg/L Br2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



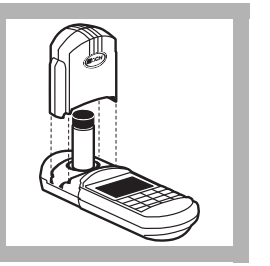
6. Add the contents of one DPD Total Chlorine Powder Pillow to the sample cell (the prepared sample). Cap the cell and swirl vigorously to dissolve the powder.

Note: *It is not necessary that all the powder dissolves. A pink color will develop if bromine is present.*

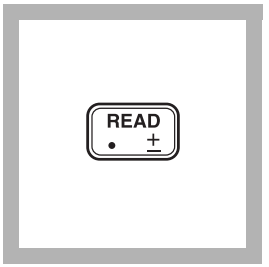


7. Press:**TIMER ENTER**

A three-minute reaction period will begin.



8. When the timer beeps, place the sample into the cell holder. Tightly cover the sample cell with the instrument cap.



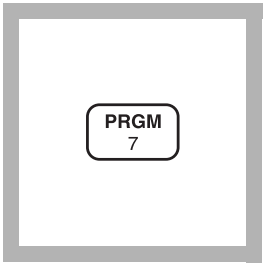
9. Press: **READ**

The cursor will move to the right, then the result in mg/L bromine will be displayed.

Note: *If samples temporarily turn yellow after reagent addition, or the display flashes "limit", it is due to high bromine levels. Dilute fresh samples and repeat the test. A slight loss of bromine may occur during dilution. Multiply results by the dilution factor; see Section 1.*

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Using AccuVac Ampuls



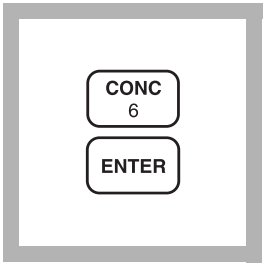
1. Enter the stored program number for bromine (Br_2) AccuVac Ampuls.

Press: **PRGM**

The display will show:

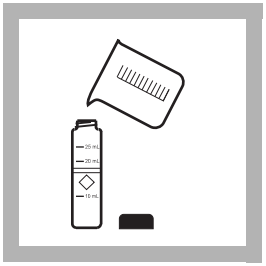
PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



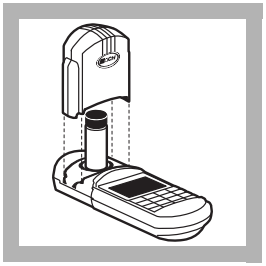
2. Press: **6 ENTER**

The display will show **mg/L, Br2** and the **ZERO** icon**.**

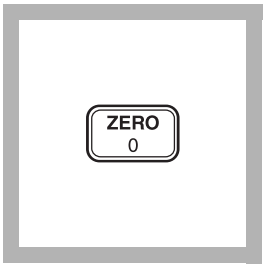


3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

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



4. Place the blank in the cell holder. Tightly cover the sample cell with the instrument cap.

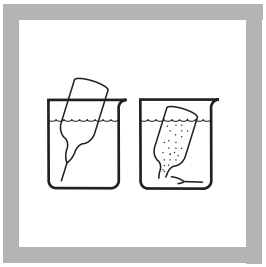


5. Press: **ZERO**

The cursor will move to the right, then the display will show:

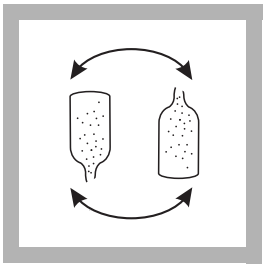
0.00 mg/L Br2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



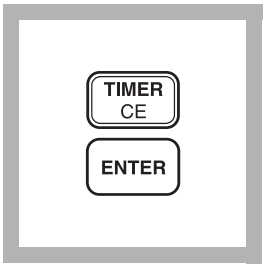
6. Fill one DPD Total Chlorine Reagent AccuVac Ampul with sample.

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



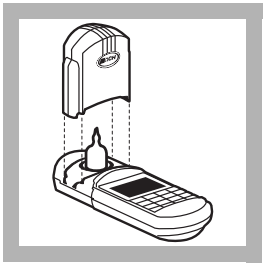
7. Quickly invert the ampule several times to mix. Wipe off any liquid or fingerprints.

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

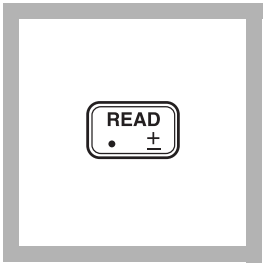


8. Press: **TIMER ENTER**

A three-minute reaction period will begin.



9. After the timer beeps, place the AccuVac ampul into the cell holder. Tightly cover the ampule with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L bromine will be displayed.

Note: *If the sample temporarily turns yellow after reagent addition, or the display flashes "limit", it is due to high bromine levels. Dilute a fresh sample and repeat the test. A slight loss of bromine may occur during dilution. Multiply the result by the dilution factor; see Section 1.*

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Analyze samples for bromine **immediately** after collection.

Avoid plastic containers since these may have a large bromine demand. **Pretreat glass** sample containers to remove any bromine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pretreatment is necessary.

A common error in testing for bromine is introduced when a representative sample is not obtained. If sampling from a tap, let the sample flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark.

Perform the bromine analysis immediately after collection.

Accuracy Check

Standard Additions Method (using powder pillows)

a) Snap the top off a LR Chlorine PourRite® Ampule Standard Solution.

b) Use a TenSette Pipet to add 0.1 mL of the standard to the reacted sample (this is the spiked sample). Swirl to mix.

c) Re-zero the instrument using the original sample (the blank).

d) Place the spiked sample in the cell holder and press **READ**. Record the result.

e) Calculate the equivalent concentration of mg/L bromine added to the sample:

$$\text{mg/L Bromine added} = \frac{0.1\ (\text{vol. standard added}) \times \text{Label value (mg/L Chlorine)} \times 2.25}{10.1\ (\text{sample + standard volume})}$$

f) The spiked sample result (step d) should reflect the analyzed sample result + the calculated mg/L Br_2 added (step e).

g) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Standard Additions Method (using AccuVac Ampuls)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution.

b) Use a graduated cylinder to measure 25 mL of sample into each of two beakers.

c) Use a TenSette Pipet to add 0.2 mL of the standard to one of the beakers (this is the spiked sample). Swirl to mix.

d) Fill a DPD Total Chlorine AccuVac completely from each beaker.

e) Analyze the spiked and unspiked sample as described in the procedure.

f) Calculate the equivalent concentration of mg/L bromine added to the sample:

$$\text{mg/L Bromine added} = \frac{0.2\ (\text{vol. standard added}) \times \text{Label value (mg/L Chlorine)} \times 2.25}{25.2\ (\text{sample + standard volume})}$$

g) The spiked sample result should reflect the analyzed sample result + the calculated mg/L Br_2 added (step f).

h) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Method Performance

Precision

In a single laboratory using a standard solution of 2.34 mg/L bromine and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.02 mg/L bromine.

In a single laboratory using a standard solution of 2.31 mg/L bromine and two representative lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation ± 0.02 mg/L bromine.

Estimated Detection Limit

The estimated detection limit for program 5 is 0.04 mg/L Br_2 and 0.03 mg/L Br_2 for program 6. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Level and Treatment
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1, Correcting for Volume Additions*).
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1, Correcting for Volume Additions*).
Chlorine	Interferes at all levels
Chlorine Dioxide	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$
Iodine	Interferes at all levels
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium , Oxidized (Cr^{6+})	**1.** Adjust sample pH to 6-7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait 1 minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct bromine concentration.
Monochloramine	Interferes at all levels
Ozone	Interferes at all levels
Peroxides	May interfere
Extreme sample pH and highly buffered samples	Adjust to pH 6-7. See *Interferences, Section 1*.

Summary of Method

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

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interference will be hazardous wastes as regulated by Federal RCRA for arsenic (D004). See *Section 3* for more information on proper disposal of these materials.

REQUIRED REAGENTS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Total Chlorine Reagent Powder Pillows	1 pillow	100/pkg	21056-69

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

DPD Total Chlorine Reagent AccuVac Ampuls	1 ampule	25/pkg	25030-25

REQUIRED APPARATUS (USING POWDER PILLOWS)

Sample Cells, 10-20-25-mL, w/ cap		6/pkg	24019-06

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Beaker, 50 mL	1	each	500-41

OPTIONAL REAGENTS

Chlorine Standard Solution, PourRite ampule, 25-30 mg/L, 2 mL		20/pkg	26300-20
DPD Total Chlorine Reagent, SwifTest		250 Tests	28024-00
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 N		100 mL* MDB	1270-32
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit		each	24052-00
PourRite Ampule Breaker		each	24846-00
Cylinder, graduated, 25 mL		each	508-40
pH Meter, *sens**ion***™***1**, portable		each	51700-00
pH Indicator Paper, 1 to 11 pH units		5 rolls/pkg	391-33
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

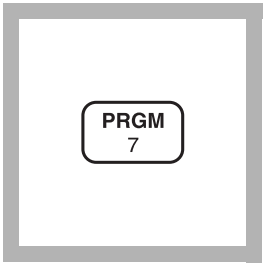
Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Contact Hach for larger sizes

DPD Method

USEPA accepted for reporting drinking water analyses*
For testing higher levels of free chlorine (hypochlorous acid and hypochlorite) in drinking water, cooling water, and industrial process waters

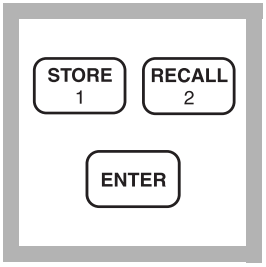
Note: *This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.*



1. Enter the user program number for Chlorine, UHR.

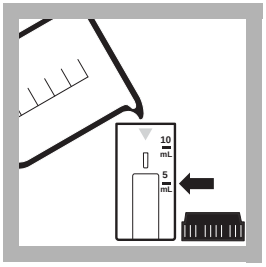
Press: **PRGM**
The display will show:
PRGM?

Note: *If the chlorine is typically less than 2.0 mg/L, use method 8021, program number 9.*

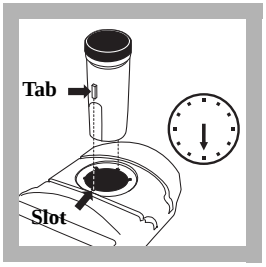


2. Press:
12 ENTER

The display will show
mg/L Cl_2
then: **ZERO**



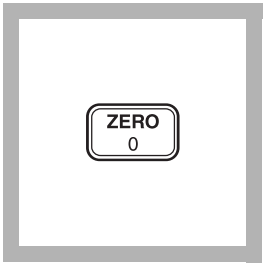
3. Fill the 10-mL/1-cm cell to the 5-mL line with sample.



4. Place the cell into the instrument. Cover the sample cell tightly with the instrument cap.

Note: *Place the cell into the cell holder as illustrated. The sample cell tab should be at the 6 o'clock position and completely seated in the cell holder slot.*

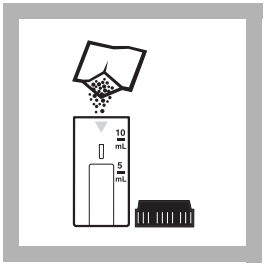
* Procedure is equivalent to USEPA method 330.5 for wastewater and Standard Method 4500-C1-G for drinking water.



5. Press: **ZERO**

The cursor will move to the right, then the display will show:

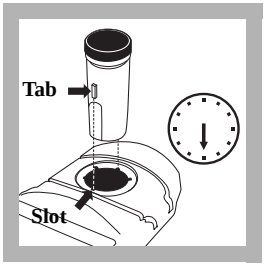
0.0 mg/L Cl_2



6. Remove the sample cell from the cell holder and add the contents of one 25-mL DPD Free Chlorine Reagent pillow to the sample. Cap and shake the sample cell about 20 seconds to dissolve.

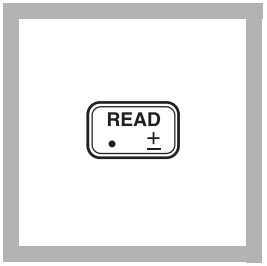
Proceed **immediately** to *step 7*.

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



7. Place the sample cell into the instrument. Cover the sample cell tightly with the instrument cap.

Note: *Place the sample cell into the cell holder as illustrated. The sample cell tab should be at the 6-o'clock position and completely seated in the cell holder slot.*



8. Within one minute after reagent addition, press: **READ**.

The cursor will move to the right. The result in mg/L chlorine (as Cl_2) will be displayed.

Note: *See "Interferences" on page 88 for samples with high monochloramine concentrations.*

Sampling and Storage

Analyze samples for chlorine immediately after collection. Free chlorine is a strong oxidizing agent and reacts rapidly with various compounds. Many factors such as sunlight, pH, temperature, and sample composition will influence decomposition of free chlorine in water.

- Avoid plastic containers which may have a large chlorine demand.
- Pretreat glass sample containers to remove chlorine demand by soaking in a dilute bleach solution (1 mL of commercial bleach to 1 liter of deionized water) for at least one hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.
- Use separate, dedicated sample cells for free and total chlorine determinations. If trace iodide from the total chlorine reagent is carried over to the free chlorine test, monochloramine could interfere.

- A common error in testing for chlorine is failure to obtain a representative sample. If sampling from a tap, let the water flow for at least five minutes to ensure a representative sample. Let the sample container overflow with sample several times. Cap the container so there is no air above the sample.
- If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 5-mL mark. Proceed with the chlorine test immediately.

Accuracy Check

1. Fill three mixing cylinders (Cat. No. 20886-38) with 5-mL of sample.
2. Snap the neck of a HR Chlorine Ampule Standard, 50–75 mg/L Cl_2. Using the TenSette® Pipet, add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to each cylinder and mix thoroughly.
3. Analyze each standard addition sample as described in the procedure. Record each result.
4. Calculate the concentration of mg/L chlorine added to each sample.

$$\text{mg/L chlorine added} = \frac{\text{volume of standard added} \times \text{label value of } Cl_2 \text{ standard ampule}}{\text{sample volume} + \text{volume of standard added}}$$

The spiked sample results should reflect the analyzed sample result plus the calculated mg/L Cl_2 added to each sample. If these increases do not occur, see Standard Additions in Section 1 of a DR/800 Procedure Manual for more information.

Method Performance

Precision

In a single laboratory, using a chlorine standard solution of 5.05 mg/L Cl_2 and representative lots of reagent, a single operator obtained a standard deviation of ± 0.05 mg/L Cl_2.

Estimated Detection Limit

The estimated detection limit for Method 10069 is 0.1 mg/L Cl_2. For more information on the estimated detection limit, see Section 1 of the DR/800 Procedure Manual.

Interferences

Interfering Substance	Interference Levels and Treatments
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. **1.** Neutralize to pH 6–7 with 1 N Sodium Hydroxide. **2.** Determine amount to be added on a separate sample aliquot, then add the same amount to the sample being tested. **3.** Correct for volume addition.
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. **1.** Neutralize to pH 6–7 with 1 N Sulfuric Acid. **2.** Determine amount to be added on a separate sample aliquot, then add the same amount to the sample being tested. **3.** Correct for volume addition.
Bromine, Br_2	Interferes at all levels
Chlorine Dioxide, ClO_2	Interferes at all levels
Chloramines, organic	May interfere
Iodine, I_2	Interferes at all levels
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium, oxidized (Cr^{6+})	**1.** Adjust sample pH to 6–7. **2.** Add 2 drops Potassium Iodide (30 g/L) to a 5-mL sample. **3.** Mix and wait 1 minute. **4.** Add 2 drops of Sodium Arsenite (5 g/L) and mix. **5.** Analyze the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.

<table>
<tr><th>Interfering Substance</th><th>Interference Levels and Treatments</th></tr>
<tr><td>Monochloramine</td><td>For conventional free chlorine disinfection (beyond the breakpoint), monochloramine concentrations are very low. If monochloramine is present in the sample, its interference in the free chlorine test varies with the sample temperature, the relative amount of monochloramine to free chlorine, and the time required to do the analysis. Approximate interference levels of monochloramine in the free chlorine test are listed below (as mg/L Cl_2).
<table>
<tr><th>NH_2Cl</th><th colspan="4">Sample Temperature °C (°F)</th></tr>
<tr><th>(as Cl_2)</th><th>5 (40)</th><th>10 (50)</th><th>20 (68)</th><th>30(83)</th></tr>
<tr><td>1.2</td><td>0.2</td><td>0.2</td><td>0.3</td><td>0.3</td></tr>
<tr><td>2.5</td><td>0.4</td><td>0.5</td><td>0.6</td><td>0.6</td></tr>
<tr><td>3.5</td><td>0.5</td><td>0.6</td><td>0.7</td><td>0.8</td></tr>
</table></td></tr>
<tr><td>Ozone</td><td>Interferes at all levels</td></tr>
<tr><td>Peroxides</td><td>May interfere</td></tr>
<tr><td>Extreme sample pH or highly buffered samples</td><td>Adjust the sample pH to 6–7 with Sulfuric Acid or Sodium Hydroxide</td></tr>
</table>

Summary of Method

The range of analysis using the DPD method for free chlorine can be extended by adding more indicator in proportion to sample volume. Thus, a larger fill powder pillow of DPD Free Chlorine Reagent is added to a 5-mL sample portion.

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

Instrument Setup

The following procedure will add this method as a new Hach program to a DR/800 instrument.

1. Turn on the instrument by pressing the **ON** key.
2. Press the **SETUP** key.
3. Press the **DOWN** arrow key until the prompt line shows USER.
4. Press the **ENTER** key.
5. Enter “8138”, followed by **ENTER**.

6. Key the number in the "Enter" column corresponding to line number 1 on the display. Press **ENTER**. Repeat for lines 2–56 on the display.

Line Number	Enter	Line Number	Enter
1	12	29	0
2	24	30	0
3	73	31	0
4	0	32	0
5	0	33	0
6	0	34	0
7	0	35	0
8	62	36	0
9	55	37	0
10	23	38	0
11	88	39	0
12	64	40	0
13	113	41	0
14	242	42	0
15	18	43	0
16	0	44	110
17	0	45	0
18	0	46	0
19	0	47	10
20	67	48	0
21	108	49	180
22	50	50	0
23	0	51	0
24	0	52	0
25	0	53	0
26	0	54	236
27	0	55	0
28	0	56	255

REQUIRED REAGENTS

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

REQUIRED APPARATUS

Sample Cell, 10-mL/1-cm	1	2/pkg	48643-02

OPTIONAL REAGENTS

Chlorine Standard Solution, 2-mL Voluette® Ampule, 50–75 mg/L		20/pkg	14268-20
Potassium Iodide Solution, 30-g/L		100 mL MDB	343-32
Sodium Arsenite Solution, 5-g/L		100 mL MDB	1047-32
Sodium Hydroxide Standard Solution, 1.00 N		100 mL MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N		100 mL MDB	1270-32
Water, deionized		4 L	272-56

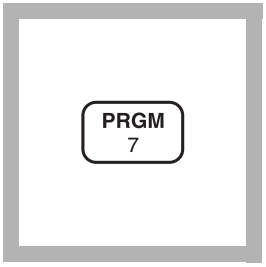
OPTIONAL APPARATUS

Ampule Breaker Kit		each	24846-00
Cylinder, graduated, 10-mL, mixing		each	20886-38
pH Meter, sens***ion***™1, portable, with electrode		each	51700-10
Pipet, TenSette®, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28

CHLORINE, TOTAL, Ultra-High Range (0.0–10.0 mg/L Cl_2) Method 10070

DPD Method **USEPA accepted for reporting water and wastewater analyses***
For testing higher levels of total chlorine (free and combined) in drinking water, cooling water, industrial process waters, or treated wastewater

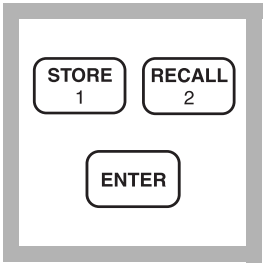
Note: *This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.*



1. Enter the user program number for Chlorine, UHR.

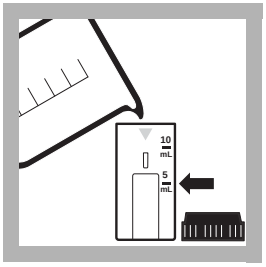
Press: **PRGM**
The display will show:
PRGM?

Note: *If the chlorine is typically less than 2.0 mg/L, use method 8167, program number 9.*

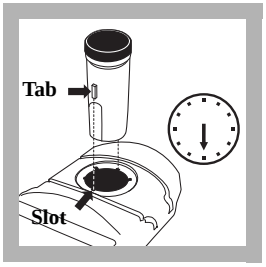


2. Press:
12 ENTER

The display will show
mg/L Cl_2
then: **ZERO**



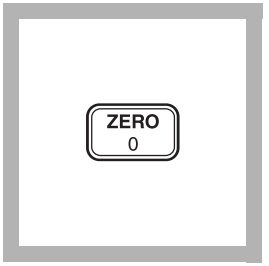
3. Fill the 10-mL/1-cm cell to the 5-mL line with sample.



4. Place the sample cell into the instrument. Cover the sample cell tightly with the instrument cap.

Note: *Place the cell into the cell holder as illustrated. The sample cell tab should be at the 6 o'clock position and completely seated in the cell holder slot.*

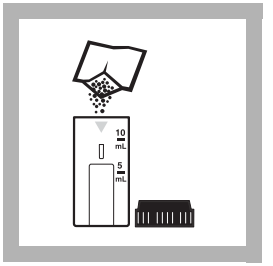
* Procedure is equivalent to USEPA method 330.5 for wastewater and Standard Method 4500-C1-G for drinking water.



5. Press: **ZERO**

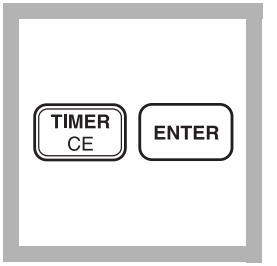
The cursor will move to the right, then the display will show:

0.0 mg/L Cl_2



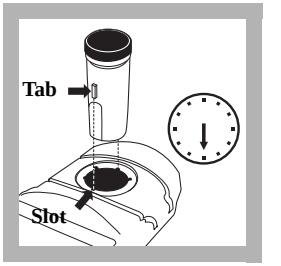
6. Remove the sample cell from the cell holder and add the contents of one 25- mL DPD Total Chlorine Reagent pillow to the sample. Cap and shake the sample cell about 20 seconds to dissolve.

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



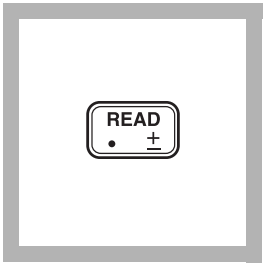
7. Press:
TIMER ENTER

A 3-minute reaction period will begin.



8. Within 3 minutes after the timer beeps, place the sample cell into the instrument. Cover the sample cell tightly with the instrument cap.

Note: *Place the cell into the cell holder as illustrated. The sample cell tab should be at the 6-o'clock position and completely seated in the cell holder slot.*



9. Press: **READ**

The cursor will move to the right. The result in mg/L chlorine (as Cl_2) will be displayed.

Sampling and Storage

Analyze samples for chlorine immediately after collection. Free and combined chlorine are strong oxidizing agents and react rapidly with various compounds. Many factors such as sunlight, pH, temperature, and sample composition will influence decomposition of chlorine in water.

- Avoid plastic containers which may have a large chlorine demand.
- Pretreat glass sample containers to remove chlorine demand by soaking in a dilute bleach solution (1 mL of commercial bleach to 1 liter of deionized water) for at least one hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.
- Use separate, dedicated sample cells for free and total chlorine determinations. If trace iodide from the total chlorine reagent is carried over to the free chlorine test, monochloramine could interfere.
- A common error in testing for chlorine is failure to obtain a representative sample. If sampling from a tap, let the water flow for at least five minutes to ensure a representative sample. Let the sample container overflow with sample several times. Cap the container so there is no air above the sample.
- If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 5-mL mark. Proceed with the chlorine test immediately.

Accuracy Check

1. Fill three mixing cylinders (Cat. No. 20886-38) with 5-mL of sample.

2. Snap the neck of a HR Chlorine Ampule Standard, 50–75 mg/L Cl_2. Using the TenSette® Pipet, add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to each cylinder and mix thoroughly.

3. Analyze each standard addition sample as described in the procedure. Record each result.

4. Calculate the concentration of mg/L chlorine added to each sample.

$$\text{mg/L chlorine added} = \frac{\text{volume of standard added} \times \text{label value of } Cl_2 \text{ standard ampule}}{\text{sample volume + volume of standard added}}$$

The spiked sample results should reflect the analyzed sample result plus the calculated mg/L Cl_2 added to each sample. If these increases do not occur, see Standard Additions in Section 1 of a DR/800 Procedure Manual for more information.

Method Performance

Precision

In a single laboratory, using a chlorine standard solution of 5.05 mg/L Cl_2 and representative lots of reagent, a single operator obtained a standard deviation of ± 0.05 mg/L Cl_2.

Estimated Detection Limit

The estimated detection limit for Method 10070 is 0.05 mg/L Cl_2. For more information on the estimated detection limit, see Section 1 of a DR/800 Procedure Manual.

Interferences

Interfering Substance	Interference Levels and Treatments
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. **1.** Neutralize to pH 6–7 with 1 N Sodium Hydroxide. **2.** Determine amount to be added on a separate sample aliquot, then add the same amount to the sample being tested. **3.** Correct for volume addition.
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. **1.** Neutralize to pH 6–7 with 1 N Sulfuric Acid. **2.** Determine amount to be added on a separate sample aliquot, then add the same amount to the sample being tested. **3.** Correct for volume addition.
Bromine, Br_2	Interferes at all levels
Chlorine Dioxide, ClO_2	Interferes at all levels
Chloramines, organic	May interfere
Iodine, I_2	Interferes at all levels

Interfering Substance	Interference Levels and Treatments
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium, oxidized (Cr^{6+})	**1.** Adjust sample pH to 6–7. **2.** Add 2 drops Potassium Iodide (30 g/L) to a 5-mL sample. **3.** Mix and wait 1 minute. **4.** Add 2 drops of Sodium Arsenite (5 g/L) and mix. **5.** Analyze the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.
Ozone	Interferes at all levels
Peroxides	May interfere
Extreme sample pH or highly buffered samples	Adjust the sample pH to 6–7 with Sulfuric Acid or Sodium Hydroxide

Summary of Method

The range of analysis using the DPD method for total chlorine can be extended by adding more indicator in proportion to sample volume. Thus, a larger fill powder pillow of DPD Total Chlorine Reagent is added to a 5-mL sample portion.

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 pink color which is proportional in intensity to the total chlorine concentration.

Instrument Setup

The following procedure will add this method as a new Hach program to a DR/800 instrument.

1. Turn on the instrument by pressing the **ON** key.

2. Press the **SETUP** key.

3. Press the **DOWN** arrow key until the prompt line shows USER.

4. Press the **ENTER** key.

5. Enter “8138”, followed by **ENTER**.

6. Key the number in the “Enter” column corresponding to line number 1 on the display. Press **ENTER**. Repeat for lines 2–56 on the display.

Line Number	Enter	Line Number	Enter
1	12	29	0
2	24	30	0
3	73	31	0
4	0	32	0
5	0	33	0
6	0	34	0
7	0	35	0
8	62	36	0
9	55	37	0
10	23	38	0
11	88	39	0
12	64	40	0
13	113	41	0
14	242	42	0
15	18	43	0
16	0	44	110
17	0	45	0
18	0	46	0
19	0	47	10
20	67	48	0
21	108	49	180
22	50	50	0
23	0	51	0
24	0	52	0
25	0	53	0
26	0	54	236
27	0	55	0
28	0	56	255

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Total Chlorine Reagent Powder Pillows, 25-mL	1	100/pkg	14064-99

REQUIRED APPARATUS

Sample Cell, 10-mL/1-cm	1	2/pkg	48643-02

OPTIONAL REAGENTS

Chlorine Standard Solution, 2-mL Voluette® Ampule, 50–75 mg/L		20/pkg	14268-20
Potassium Iodide Solution, 30-g/L		100 mL MDB	343-32
Sodium Arsenite Solution, 5-g/L		100 mL MDB	1047-32
Sodium Hydroxide Standard Solution, 1.00 N		100 mL MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N		100 mL MDB	1270-32
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

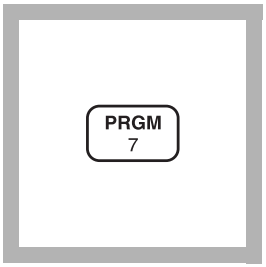
Ampule Breaker Kit		each	24846-00
Cylinder, graduated, 10-mL, mixing		each	20886-38
pH Meter, sens***ion***™1, portable, with electrode		each	51700-10
Pipet, TenSette®, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28

CHLORINE, FREE (0 to 2.00 mg/L)

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

Note: *This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.*

Using Powder Pillows



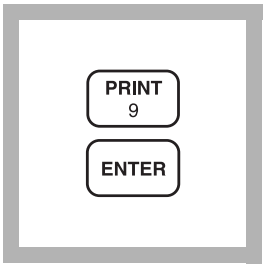
1. Enter the stored program number for free and total chlorine (Cl_2) powder pillows.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



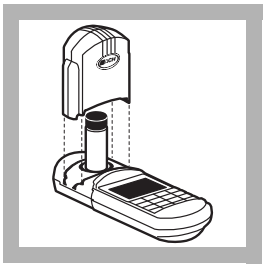
2. Press: **9 ENTER**

The display will show **mg/L, Cl2** and the **ZERO** icon.

3. Fill a sample cell with 10 mL of sample (the blank).

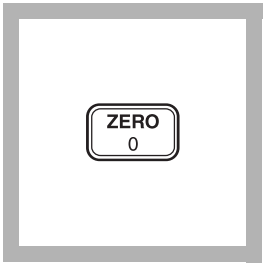
Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

Note: *The SwifTest Dispenser for Free Chlorine can be used in place of the powder pillows in step 7.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

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

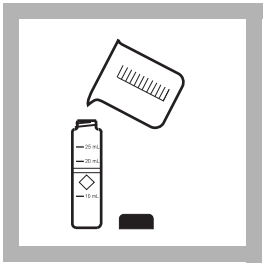


5. Press: **ZERO**

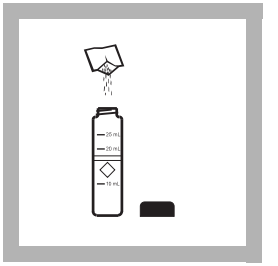
The cursor will move to the right, then the display will show:

0.00 mg/L Cl2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*

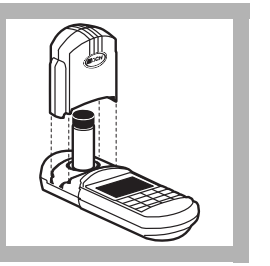


6. Fill another cell with 10 mL of sample.



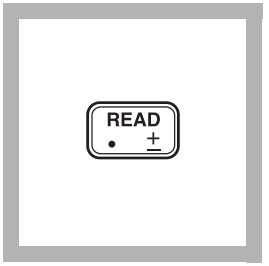
7. Add the contents of one DPD Free Chlorine Powder Pillow to the sample cell (the prepared sample). Cap the cell and swirl vigorously to dissolve the powder.

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



8. Immediately place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *Perform Step 9 within one minute of reagent addition.*



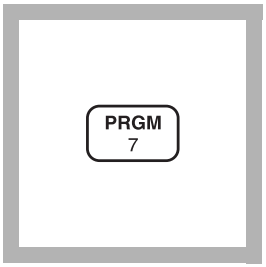
9. Press: **READ**

The cursor will move to the right, then the result in mg/L chlorine will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Note: *If the sample temporarily turns yellow after reagent addition, or the display flashes "limit", it is due to high chlorine levels. Dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the dilution factor; see Section 1. Or, use the High Range Free Chlorine test, program #8.*

Using AccuVac Ampuls



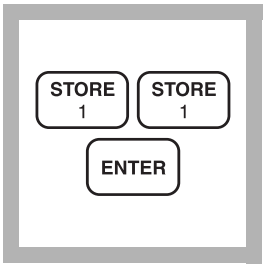
1. Enter the stored program number for free and total chlorine (Cl_2)-AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

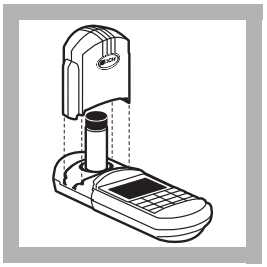


2. Press: **11 ENTER**

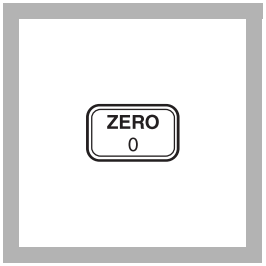
The display will show **mg/L, Cl2** and the **ZERO** icon.

3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

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



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

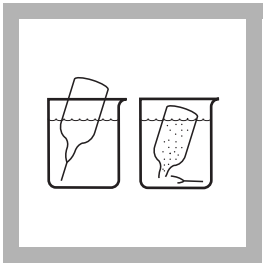


5. Press: **ZERO**

The cursor will move to the right, then the display will show:

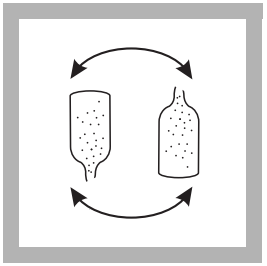
0.00 mg/L Cl2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



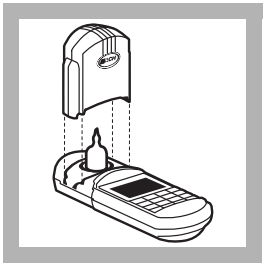
6. Fill a DPD Free Chlorine Reagent AccuVac Ampul with sample.

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



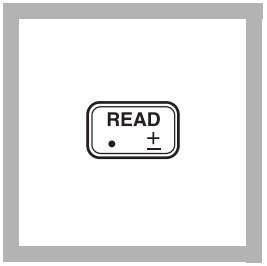
7. Quickly invert the ampule several times to mix. Wipe off any liquid or fingerprints.

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



8. Immediately place the AccuVac Ampul into the cell holder. Tightly cover the ampule with the instrument cap.

Note: *Perform step 9 within one minute of reagent addition.*



9. Press: **READ**

The cursor will move to the right, then the result in mg/L chlorine will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Note: *If the sample temporarily turns yellow after reagent addition, or the display flashes "limit", it is due to high chlorine levels. Dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the dilution factor; see Section 1.*

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free chlorine is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinity influence decomposition of free chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pretreatment is necessary.

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

A common error in testing for chlorine is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Perform the analysis immediately.

Accuracy Check

Standard Additions Method (using powder pillows)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution.

b) Use a TenSette Pipet to add 0.1 mL of the standard to the reacted sample (this is the spiked sample). Swirl to mix.

c) Re-zero the instrument using the original sample (the blank).

d) Place the spiked sample in the cell holder and press **READ**. Record the results.

e) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L Chlorine added} = \frac{0.1(\text{vol. standard added}) \times \text{Label value (mg/L } Cl_2)}{10.1(\text{sample + standard volume})}$$

f) The spiked sample result (step d) should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step e).

g) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Standard Additions Method (using AccuVac Ampuls)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution.

b) Use a graduated cylinder to measure 25 mL of sample into each of two beakers.

c) Use a TenSette Pipet to add 0.2 mL of the standard to one of the beakers (this is the spiked sample). Swirl to mix.

d) Fill a DPD Free Chlorine AccuVac completely from each

beaker.

e) Analyze the spiked and unspiked sample as described in the procedure.

f) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L Chlorine added} = \frac{0.2(\text{vol. standard added}) \times \text{Label value (mg/L } Cl_2)}{25.2(\text{sample + standard volume})}$$

g) The spiked sample result should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step f).

h) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Method Performance

Precision

In a single laboratory using a standard solution of 1.00 mg/L chlorine and two representative lots of reagents with the instrument, a single operator obtained a standard deviation of ±0.01 mg/L chlorine.

In a single laboratory using a standard solution of 1.00 mg/L chlorine and two representative lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation of ±0.01 mg/L chlorine.

Estimated Detection Limit (EDL)

The estimated detection limit for programs 9 and 11 is 0.02 mg/L Cl_2. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by Federal RCRA for arsenic (D004). See *Section 3* for more information on proper disposal of these materials.

Interferences

Interfering Substance	Interference Level and Treatment
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1, Correcting for Volume Additions*).
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1, Correcting for Volume Additions*).
Bromine	Interferes at all levels
Chlorine Dioxide	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$
Iodine	Interferes at all levels
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium , Oxidized (Cr^{6+})	**1.** Adjust sample pH to 6-7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.
Monochloramine	Causes a gradual drift to higher readings. When read within 1 minute after reagent addition, 3 mg/L monochloramine causes less than a 0.1 mg/L increase in the reading.
Ozone	Interferes at all levels
Peroxides	May interfere
Extreme sample pH and highly buffered samples	Adjust to pH 6-7. See *Interferences, Section 1*.

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 magenta color which is proportional to the chlorine concentration.

REQUIRED REAGENTS & APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Free Chlorine Powder Pillows, 10 mL	1 pillow	100/pkg	21055-69
Sample Cell, 10, 20, 25 mL, w/ cap	2	6/pkg	24019-06

REQUIRED REAGENTS & APPARATUS (Using AccuVac Ampuls)

DPD Free Chlorine Reagent AccuVac Ampuls	1 ampul	25/pkg	25020-25
Beaker, 50 mL	1	each	500-41H

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Chlorine Standard Solution, PourRite ampule, 25-30 mg/L, 2 mL	20/pkg	26300-20
DPD Free Chlorine Reagent, SwifTest	250 tests	28023-00
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, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Cylinder, graduated, 25 mL	each	508-40
pH Meter, *sens**ion***™***1***, portable, with electrode	each	51700-10
pH Paper, 1 to 11 pH units	5 rolls/pkg	391-33
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96Pipet
Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
PourRite Ampule Breaker	each	24846-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Marked Dropper Bottle - contact Hach for larger sizes.

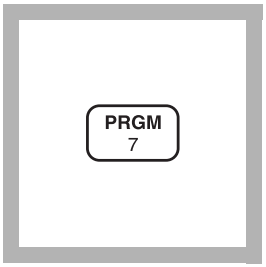
CHLORINE, TOTAL (0 to 2.00 mg/L)

DPD Method (Powder Pillows or AccuVac Ampuls)

USEPA accepted for reporting water and wastewater analyses*

Note: *This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.*

Using Powder Pillows



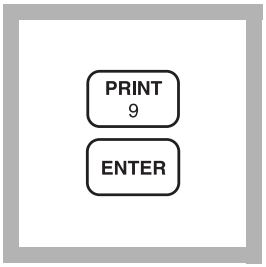
1. Enter the stored program number for total chlorine (Cl_2) powder pillows.

Press: **PRGM**

The display will show:

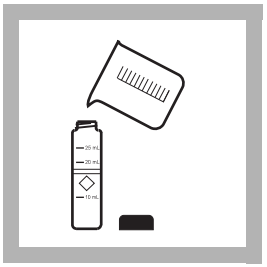
PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



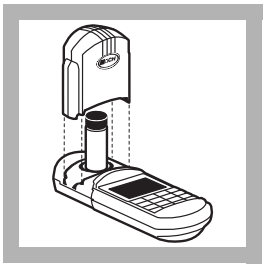
2. Press: **9 ENTER**

The display will show **mg/L, Cl2** and the **ZERO** icon**.**



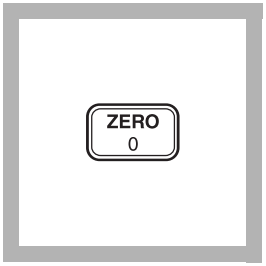
3. Fill a sample cell with 10 mL of sample (the blank).

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



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

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

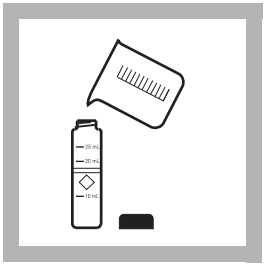


5. Press: **ZERO**

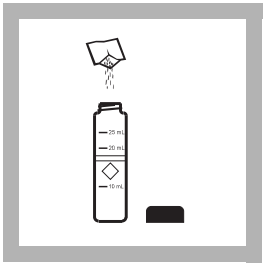
The cursor will move to the right, then the display will show:

0.00 mg/L Cl2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*

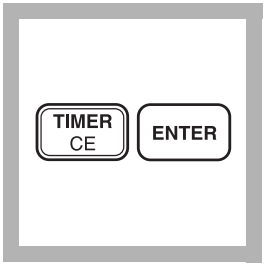


6. Fill a second cell to the 10-mL mark with sample.



7. Add the contents of one DPD Total Chlorine Powder Pillow to the sample cell (the prepared sample). Cap and swirl the sample cell vigorously to dissolve the powder.

Note: *It is not necessary that all the powder dissolves.*

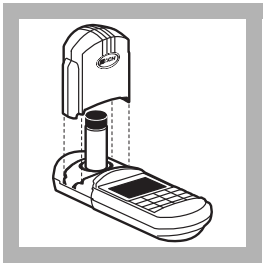


8. Press:

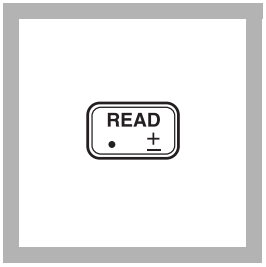
TIMER ENTER

A three-minute reaction period will begin. A pink color will develop if chlorine is present.

Note: *The SwifTest Dispenser for Total Chlorine can be used in place of the powder pillows in step 7.*



9. After the timer beeps, place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



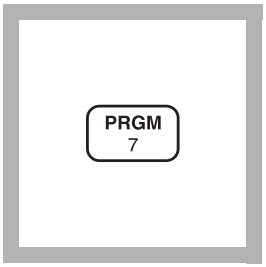
10. Press: **READ**

The cursor will move to the right, then the result in mg/L total chlorine will be displayed.

Note: *It the sample temporarily turns yellow after sample addition, or the display flashes "limit", it is due to high chlorine levels. Dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the dilution factor; see Section 1. Or use the High Range Total Chlorine test, program #8.*

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Using AccuVac Ampuls



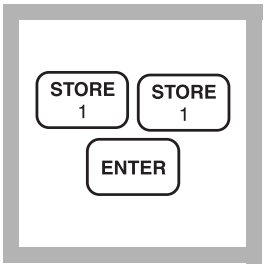
1. Enter the stored program number for total chlorine (Cl_2) AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

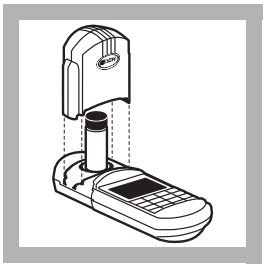


2. Press: **11 ENTER**

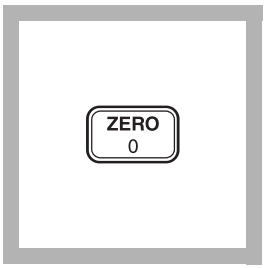
The display will show **mg/L, Cl2** and the **ZERO** icon**.**

3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

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



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

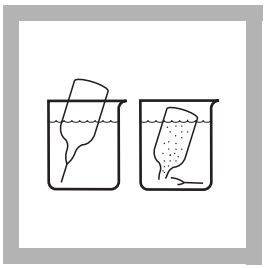


5. Press: **ZERO**

The cursor will move to the right, then the display will show:

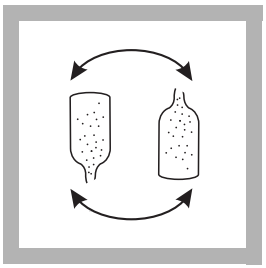
0.00 mg/L Cl2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



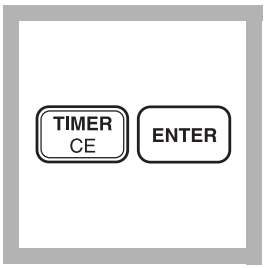
6. Fill a DPD Total Chlorine Reagent AccuVac Ampul with sample.

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



7. Quickly invert the ampule several times to mix. Wipe off any liquid or fingerprints.

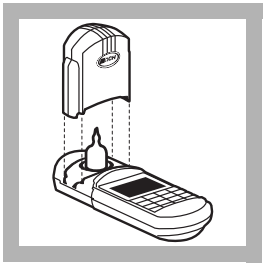
Note: *A pink color will form if chlorine is present.*



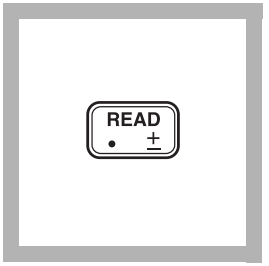
8. Press:

TIMER ENTER

A three-minute reaction period will begin.



9. When the timer beeps, place the AccuVac Ampul into the cell holder. Tightly cover the ampule with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L total chlorine will be displayed.

Note: *If the sample temporarily turns yellow after sample addition, or the display shows "limit", it is due to high chlorine levels. Dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the appropriate dilution factor; see Section 1.*

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free chlorine is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence decomposition of chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

A common error in testing for chlorine is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Perform the chlorine analysis immediately.

Accuracy Check

Standard Additions Method (using powder pillows)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution.

b) Use a TenSette Pipet to add 0.1 mL of the standard to the reacted sample (this is the spiked sample). Swirl to mix.

c) Re-zero the instrument using the original sample (the blank).

d) Place the spiked sample into the cell holder and press **READ**. Record the results.

e) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L chlorine added} = \frac{0.1\ (\text{vol. standard added}) \times \text{Label value (mg/L } Cl_2)}{10.1(\text{sample + standard volume})}$$

f) The spiked sample result (step d) should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step e).

g) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Standard Additions Method (using AccuVac Ampuls)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution.

b) Use a graduated cylinder to measure 25 mL of sample into

each of two beakers.

c) Use a TenSette Pipet to add 0.2 mL of the standard to one of the beakers (this is the spiked sample). Swirl to mix.

d) Fill a DPD Total Chlorine AccuVac completely from each beaker.

e) Analyze the spiked and unspiked sample as described in
the procedure.

f) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L chlorine added} = \frac{0.2\ (\text{vol. standard added}) \times \text{Label value (mg/L Chlorine)}}{25.2\ (\text{sample + standard volume})}$$

g) The spiked sample result should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step f).

h) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Method Performance

Precision

In a single laboratory, using a standard solution of 1.00 mg/L chlorine and two lots of reagents with the instrument, a single operator obtained standard deviations of ±0.01 mg/L chlorine.

In a single laboratory, using a standard solution of 1.00 mg/L chlorine and two representative lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation of ±0.01 mg/L chlorine.

Estimated Detection Limit (EDL)

The estimated detection limit for programs 9 and 11 is 0.02 mg/L Cl_2. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Level and Treatment
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1, Correcting for Volume Additions*).
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1, Correcting for Volume Additions*).
Bromine	Interferes at all levels
Chlorine Dioxide	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$
Iodine	Interferes at all levels
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium , Oxidized (Cr^{6+})	**1.** Adjust sample pH to 6-7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.
Ozone	Interferes at all levels
Peroxides	May interfere
Extreme sample pH and highly buffered samples	Adjust to pH 6-7. See *Interferences, Section 1*.

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 chloro derivatives.

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 free chlorine and total chlorine tests. Subtract the results of the free chlorine test from the results of the total chlorine test to obtain combined chlorine.

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by Federal RCRA for arsenic (D004). See *Section 3* for more information on proper disposal of these materials.

REQUIRED REAGENTS & APPARATUS (USING POWDER PILLOWS)

Description	Qty/Test	Unit	Cat. No.
DPD Total Chlorine Reagent Powder Pillows	1 pillow	100/pkg	21056-69
Sample Cell, 10-20-25 mL, w/caps	2	6/pkg	24019-06

REQUIRED REAGENTS & APPARATUS (USING ACCUVAC AMPULS)

DPD Total Chlorine Reagent AccuVac Ampuls	1 ampul	25/pkg	25030-25
Beaker, 50 mL	1	each	500-41H

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Chlorine Standard Solution, PourRite ampule, 25-30 mg/L Cl_2	20/pkg	26300-20
DPD Total Chlorine Reagent, SwifTest	250 tests	28024-00
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, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
PourRite Ampule Breaker	each	24846-00
Cylinder, graduated, 25 mL	each	508-40
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, *sens**ion***™*1*, portable	each	51700-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28

For Technical Assistance, Price and Ordering

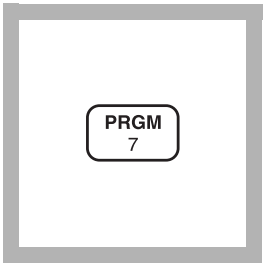
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Marked Dropper Bottle - contact Hach for larger sizes.

CHLORINE, FREE (0 to 5.00 mg/L)

DPD Test 'N Tube™ Method*

Note: *This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.*



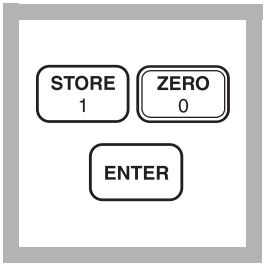
1. Enter the stored program number for Test 'N Tube free chlorine (Cl_2).

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

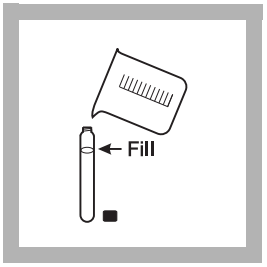


2. Press: **10 ENTER**

The display will show **mg/L, Cl2** and the **ZERO** icon**.**

3. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down fully to insert it.

Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*

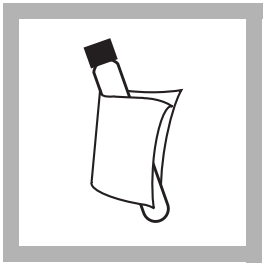


4. Fill an empty Test 'N Tube vial with sample (the blank).

Note: *Fill to the top of the Hach logo "oval" mark.*

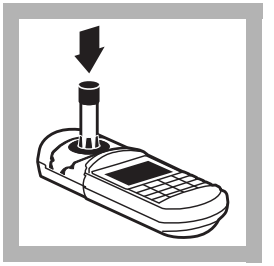
Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

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



5. Wipe the outside of the blank vial with a towel.

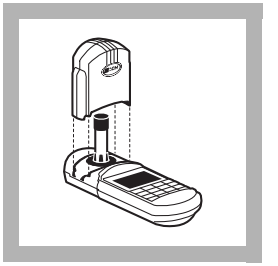
Note: *Wiping with a damp cloth followed by a dry one removes fingerprints and other marks.*



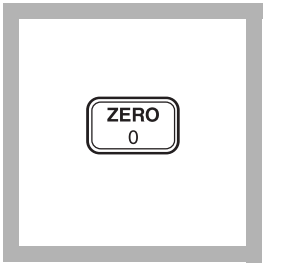
6. Place the blank in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



7. Cover the vial tightly with the instrument cap.

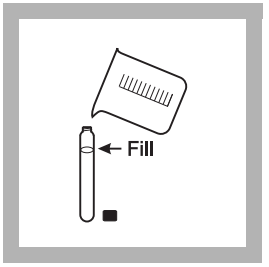


8. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L Cl2

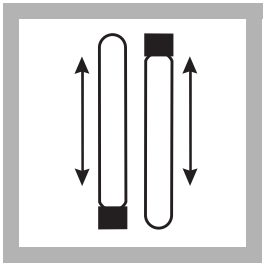
Note: *If Reagent Blank Correction is on, the display may show "limit". See Section 1.*



9. Remove the cap from a Free Chlorine DPD-TNT tube. Add 10 mL of sample.

Note: *Fill to the top of the Hach logo "oval" mark.*

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



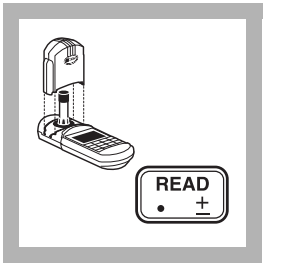
10. Cap and invert at least 10 times to dissolve the powder. This is the prepared sample.

Note: *Use slow, deliberate inversion for complete recovery. Ten inversions should take at least 30 seconds. One inversion equals turning the vial upside down, then returning it to an upright position.*

11. Within 30 seconds after mixing, wipe the prepared sample vial with a towel, then place it in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



12. Cover the vial tightly with the instrument cap.

Press: **READ**

The cursor will move to the right, then the result in mg/L free chlorine will be displayed.

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free chlorine is a strong oxidizing agent and is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinity influence decomposition of free chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pretreatment is necessary.

A common error in testing for chlorine is obtaining an unrepresentative sample. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. Perform the analysis immediately.

Accuracy Check

Standard Additions Method

a) Snap the top off a HR Chlorine PourRite™ Ampule Standard Solution.

b) Use a TenSette® Pipet to add 0.1 mL of the standard to the reacted sample (this is the spiked sample). Swirl to mix.

c) Analyze the spiked sample, beginning at Step 8 of the procedure.

d) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L chlorine added} = \frac{0.1(\text{vol. standard added}) \times \text{Label value}(\text{mg/L } Cl_2)}{10.1(\text{sample + standard volume})}$$

e) The spiked sample result (step c) should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step d).

f) If this increase does not occur, see *Standard Additions, Section 1* for more information.

Method Performance

Precision

In a single laboratory using a standard solution of 2.53 mg/L chlorine and two representative lots of reagents with the instrument, a single operator obtained a standard deviation of ±0.14 mg/L chlorine.

Estimated Detection Limit (EDL)

The estimated detection limit for program 10 is 0.03 mg/L Cl_2. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Level and Treatment
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1, Correcting for Volume Additions* in the *DR/800 Series Procedures Manual*).
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1 Correcting for Volume Additions*).
Bromine	Interferes at all levels
Chlorine Dioxide	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$
Iodine	Interferes at all levels
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium , oxidized (Cr^{6+})	**1.** Adjust sample pH to 6-7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.

<table>
<tr><th>Interfering Substance</th><th>Interference Level and Treatment</th></tr>
<tr><td>Monochloramine</td><td>For conventional free chlorine disinfection (beyond the breakpoint), typical monochloramine concentrations are very low. If monochloramine is present in the sample, its interference in the free chlorine test depends on the sample temperature, relative amount of monochloramine to free chlorine, and the time required to do the analysis. Typical interference level of monochloramine in the free chlorine test are listed below (as mg/L Cl_2).
<table>
<tr><th>NH_2Cl as Cl_2</th><th colspan="4">Sample Temp. °C (°F)</th></tr>
<tr><td></td><td>5 (40)</td><td>10 (50)</td><td>20 (68)</td><td>30 (83)</td></tr>
<tr><td>1.2 mg/L</td><td>+0.15</td><td>+0.19</td><td>+0.30</td><td>+0.29</td></tr>
<tr><td>2.5 mg/L</td><td>0.35</td><td>0.38</td><td>0.55</td><td>0.61</td></tr>
<tr><td>3.5 mg/L</td><td>0.38</td><td>0.56</td><td>0.69</td><td>0.73</td></tr>
</table></td></tr>
<tr><td>Ozone</td><td>Interferes at all levels</td></tr>
<tr><td>Peroxides</td><td>May interfere</td></tr>
<tr><td>Extreme sample pH and highly buffered samples</td><td>Adjust to pH 6-7. See Interferences, Section 1.</td></tr>
</table>

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by Federal RCRA for arsenic (D004). See *Section 3* for more information on proper disposal of these materials.

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 magenta color which is proportional to the chlorine concentration.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Test 'N Tube DPD Free Chlorine Reagent	1 vial	50/pkg	21055-45
Test 'N Tube Vials	1 vial	6/pkg	22758-06

REQUIRED APPARATUS

Caps, white	1 cap	6/pkg	22411-06
COD/TNT Adapter	1	each	48464-00

OPTIONAL REAGENTS

Chlorine Standard Solution, PourRite ampule, 50-75 mg/L, 2 mL		20/pkg	14268-20
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

OPTIONAL APPARATUS

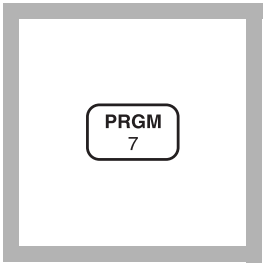
Beaker, 50 mL		each	500-41H
pH Meter, *sens**ion**™1*, portable, with electrode		each	51700-10
pH Paper, pH 1 to 11 pH		5 rolls/pkg	391-33
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
PourRite Ampule Breaker		each	24846-00
Test Tube Rack		each	18641-00

* Marked Dropper Bottle - contact Hach for larger sizes.

CHLORINE, TOTAL (0 to 5.00 mg/L)

DPD Test 'N Tube™ Method*

Note: *This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.*



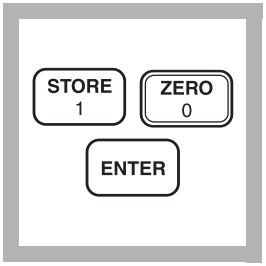
1. Enter the stored program number for Test 'N Tube total chlorine (Cl_2).

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

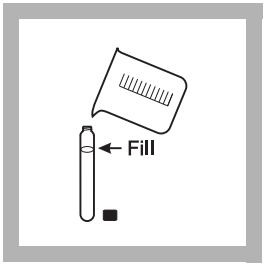


2. Press: **10 ENTER**

The display will show **mg/L, Cl2** and the **ZERO** icon**.**

3. Insert the COD/TNT Vial Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



4. Fill an empty Test 'N Tube vial with sample (the blank).

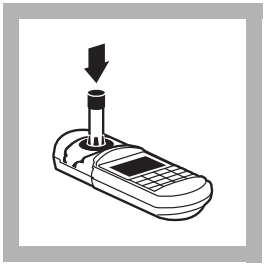
Note: *Fill to the top of the Hach logo "oval" mark.*

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

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

5. Wipe the outside of the blank vial with a towel.

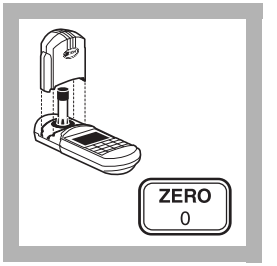
Note: *Wiping with a damp cloth followed by a dry one removes fingerprints and other marks.*



6. Place the blank in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



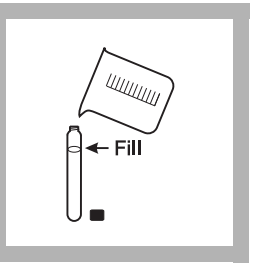
7. Cover the vial tightly with the instrument cap.

Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L Cl2

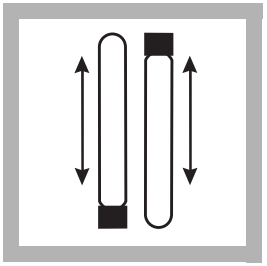
Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



8. Remove the cap from a Total Chlorine DPD-TNT tube. Add 10 mL of sample.

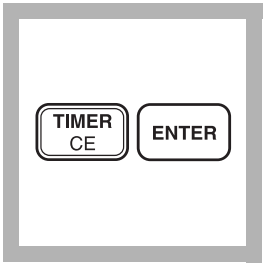
Note: *Fill to the top of the Hach logo "oval" mark.*

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



9. Cap and invert at least 10 times to dissolve the powder. This is the prepared sample.

Note: *Use slow, deliberate inversion for complete recovery. Ten inversions should take at least 30 seconds. One inversion equals turning the vial upside down, then returning it to an upright position.*

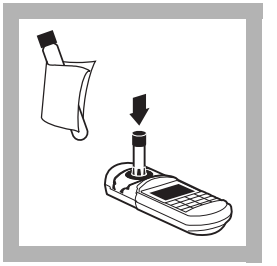


10. Press:

TIMER ENTER

A three-minute reaction period will begin.

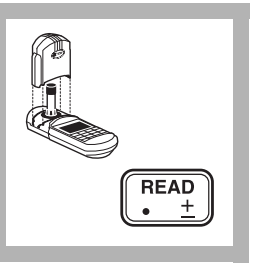
Note: *A pink color will develop if chlorine is present.*



11. When the timer beeps, wipe the prepared sample vial with a towel, then place it in the vial adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



12. Cover the vial tightly with the instrument cap.

Press: **READ**

The cursor will move to the right, then the result in mg/L total chlorine will be displayed.

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free and combined chlorine are strong oxidizing agents and are unstable in natural waters. They react rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence decomposition of chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

A common error in testing for chlorine is obtaining an unrepresentative sample. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. Perform the analysis immediately.

Accuracy Check

Standard Additions Method

a) Snap the top off a High Range Chlorine PourRite™ Ampule Standard Solution.

b) Use a TenSette® Pipet to add 0.1 mL of the standard to 10 mL of sample (this is the spiked sample). Swirl to mix.

c) Analyze the spiked sample, beginning at Step 8 of the procedure.

d) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L chlorine added} = \frac{0.1\ (\text{vol. standard added}) \times \text{Label value (mg/L } Cl_2)}{10.1(\text{sample + standard volume})}$$

e) The spiked sample result (step c) should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step d).

f) If this increase does not occur, see *Standard Additions, Section 1* for more information.

Method Performance

Precision

In a single laboratory, using a standard solution of 2.53 mg/L chlorine and two representative lots of reagents with the instrument, a single operator obtained standard deviations of ±0.14 mg/L chlorine.

Estimated Detection Limit (EDL)

The estimated detection limit for programs 10 is 0.03 mg/L Cl_2. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Level and Treatment
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Correcting for Volume Additions* in *Section 1*).
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Correcting for Volume Additions* in *Section 1*).
Bromine	Interferes at all levels
Chlorine Dioxide	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$
Iodine	Interferes at all levels
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium , oxidized (Cr^{6+})	**1.** Adjust sample pH to 6-7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.
Ozone	Interferes at all levels
Peroxides	May interfere
Extreme sample pH and highly buffered samples	Adjust to pH 6-7. See *Interferences* in *Section 1*.

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 chloro derivatives.

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 free chlorine and total chlorine tests. Subtract the results of the free chlorine test from the results of the total chlorine test to obtain combined chlorine.

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by Federal RCRA for arsenic (D004).

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Test 'N Tube DPD Total Chlorine Reagent	1 vial	25/pkg	21056-25
Test 'N Tube Vials	1 vial	6/pkg	22758-06

REQUIRED APPARATUS

COD/TNT Adapter, DR/800	1	each	48464-00

OPTIONAL REAGENTS

Chlorine Standard Solution, 2-mL PourRite ampule, 50-75 mg/L		20/pkg	14268-20
Potassium Iodide Solution, 30 g/L		100 mL*	MDB 343-32
Sodium Arsenite Solution, 5 g/L		100 mL*	MDB 1047-32
Sodium Hydroxide Standard Solution, 1.00 N		100 mL*	MDB 1045-32
Sulfuric Acid Standard Solution, 1.000 N		100 mL*	MDB 1270-32

OPTIONAL APPARATUS

Beaker, 50 mL		each	500-41H
PourRite Ampule Breaker		each	24846-00
pH Indicator Paper, pH 1 to 11		5 rolls/pkg	391-33
pH Meter, *sens**ion***™***1**, portable, with electrode		each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
Test Tube Rack		each	18641-00

* Marked Dropper Bottle - contact Hach for larger sizes.

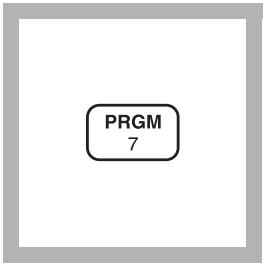
CHLORINE DIOXIDE (0 to 5.00 mg/L) Method 10126

DPD Method* **For water**

USEPA accepted for reporting for drinking water analysis

Note: *This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.*

Using Powder Pillows

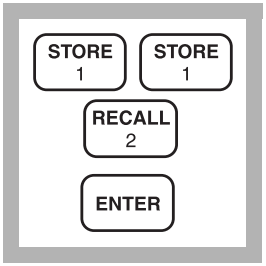


1. Enter the stored program number for chlorine dioxide (ClO_2) powder pillows.

Press: **PRGM**

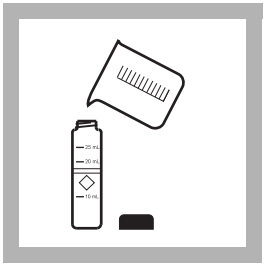
The display will show:

PRGM ?



2. Press: **112 ENTER**

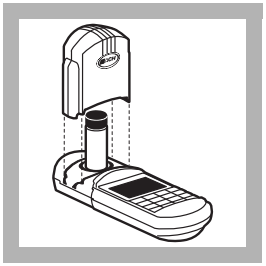
The display will show **mg/L, ClO2**, and the **ZERO** icon.



3. Fill a sample cell with 10 mL of sample (the blank).

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

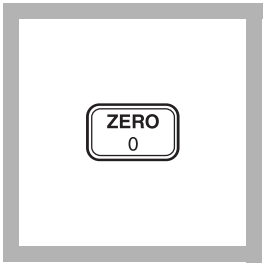
Note: *Wipe off any liquid or fingerprints before inserting the sample cell into the instrument.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *For best results, run a reagent blank using deionized water as the sample. Subtract the blank value from the sample reading to obtain the final result. See* Reagent Blank Correction *in Section 1 of the DR/800 Procedure Manual.*

* Procedure is equivalent to *Standard Method 4500, $Cl0_2P$*

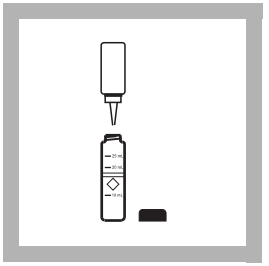


5. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L ClO2

Note: *If Reagent Blank Correction is on, the display may flash* **"limit"**. *See Section 1 of the DR/800 Procedures Manual.*

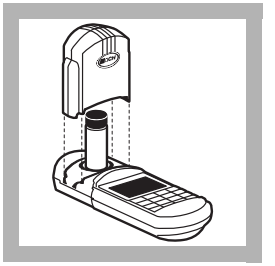


6. Add four drops of Glycine Reagent to the sample cell. Swirl to mix.

7. Add the contents of one DPD Free Chlorine Powder Pillow to the sample cell (the prepared sample). Cap the cell and swirl to mix.

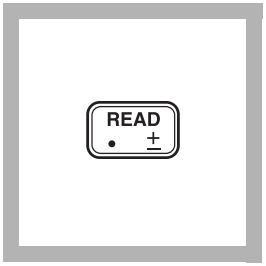
Note: *A pink color will develop if free chlorine dioxide is present.*

Note: *Perform step 9 within one minute of reagent addition.*



8. Allow 30 seconds for undissolved powder to settle. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *Wipe off any liquid or fingerprints before inserting the sample cell into the instrument.*

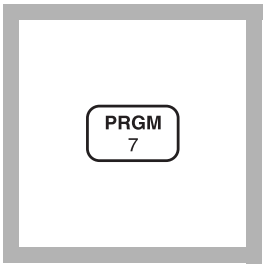


9. Press: **READ**

The cursor will move to the right, then the result in mg/L chlorine dioxide will be displayed.

Note: *If the sample temporarily turns yellow after reagent addition, or the display flashes* **"limit"**, *it is due to high chlorine dioxide levels. Dilute a fresh sample with chlorine dioxide-free water and repeat the test. A slight loss of chlorine dioxide may occur during dilution. Multiply the result by the dilution factor.*

Using AccuVac® Ampuls

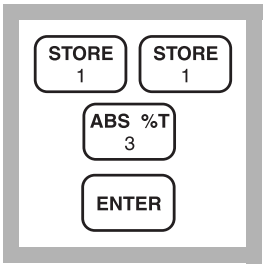


1. Enter the stored program number for chlorine dioxide (ClO_2) AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?



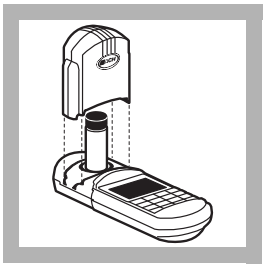
2. Press: **113 ENTER**

The display will show **mg/L, ClO2** and the **ZERO** icon.

3. Fill a sample cell with at least 10 mL of sample (the blank). Fill a 50-mL beaker with 40 mL of sample. Using the correct sample volume is important.

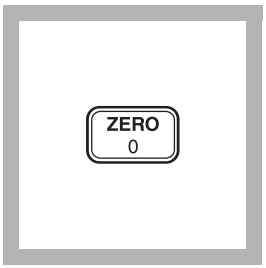
Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

Note: *Wipe off any liquid or fingerprints before inserting the sample cell into the instrument.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *For best results, run a reagent blank using deionized water as the sample. Subtract the blank value from the sample reading to obtain the final result. See* Reagent Blank Correction *in Section 1 of the DR/800 Procedure Manual.*

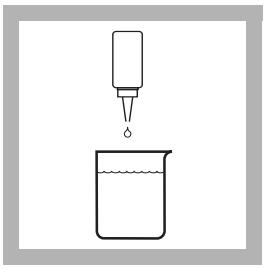


5. Press: **ZERO**

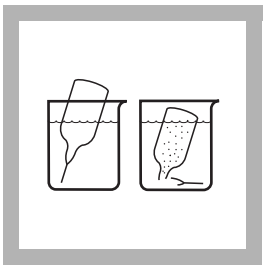
The cursor will move to the right, then the display will show:

0.00 mg/L ClO2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1 of the DR/800 Procedures Manual.*



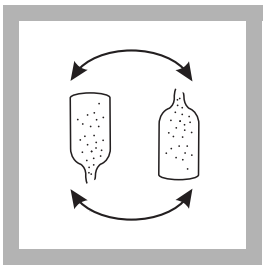
6. Add 16 drops of Glycine Reagent to the sample in the beaker. Swirl to mix.



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

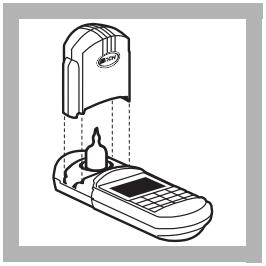
Note: *Keep the tip immersed while the ampul fills completely.*

Note: *Perform step 10 within one minute of reagent addition.*

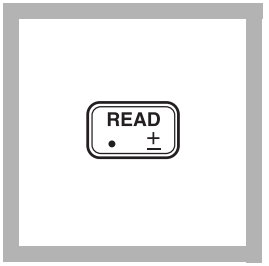


8. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

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



9. Allow 30 seconds for undissolved powder to settle. Place the AccuVac Ampul into the cell holder. Tightly cover the ampul with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L chlorine dioxide will be displayed.

Note: *If the sample temporarily turns yellow after reagent addition, or the display flashes "limit", it is due to high chlorine dioxide levels. Dilute a fresh sample with chlorine dioxide-free water and repeat the test. A slight loss of chlorine dioxide may occur during dilution. Multiply the result by the dilution factor.*

Sampling and Storage

Analyze samples for chlorine dioxide **immediately** after collection. Chlorine dioxide is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinity influence decomposition of chlorine dioxide in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine dioxide demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pretreatment is necessary.

A common error in testing for chlorine dioxide is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Perform the analysis immediately.

Accuracy Check

Because chlorine dioxide is difficult and hazardous to produce, check the DPD and glycine reagents by using chlorine standards. Proceed as follows:

1. Prepare a 1-mg/L free chlorine standard.

Method 1

a. Obtain Free Chlorine Standards, (Cat. No. 14268-10).

b. Determine the concentration of the standard from the certificate of analysis shipped with the standard (50-75 mg/L). Calculate the volume of standard needed as follows:

mL standard needed = 100 ÷ standard concentration

c. Pipet the volume of standard needed into a 100-mL volumetric flask. Dilute to the line with chlorine demand-free deionized water. Invert to mix.

Method 2

a. Dilute 1 drop of commercial 5% chlorine bleach in 1 liter of chlorine demand-free deionized water. Use this as the standard.

2. Verify the standard's concentration using the Hach Free Chlorine Method, #8021.

3. Perform the chlorine dioxide test on the standard without adding glycine (*step 6*).

4. The chlorine dioxide reading should be about 2.45 times greater than the chlorine result. If so, this verifies the DPD and the instrument are functioning properly.

5. Repeat the chlorine dioxide test on the chlorine standard, including the glycine addition (*step 6*). The reading should be less than 0.10 mg/L. This verifies that the glycine is eliminating free chlorine interference.

Method Performance

Precision

Program	Standard	95% Confidence Limits
112	0.24 mg/L	0.22–0.26 mg/L ClO_2
112	4.79 mg/L	4.67–4.91 mg/L ClO_2
113	0.26 mg/L	0.21–0.27 mg/L ClO_2
113	4.83 mg/L	4.71–4.97 mg/L ClO_2

For more information on determining precision data and method detection limits, see *Section 1* of the *DR/800 Procedures Manual*.

Estimated Detection Limit (EDL)

Program	EDL
112	0.04 mg/L ClO_2
113	0.04 mg/L ClO_2

For more information on derivation and use of Hach's estimated detection limit, see *Section 1* of the *DR/800 Procedures Manual*.

Interferences

A substance interferes if it changes the final reading by 0.1 mg/L ClO_2 or more.

Interfering Substance	Interference Levels and Treatments
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6–7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (see *Section 1, Correction For Volume Additions, in the DR/800 Procedures Manual).*
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6–7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (see *Section 1, Correction For Volume Additions, in the DR/800 Procedures Manual).*
Bromine, Br_2	Interferes at all levels.
Chlorine, Cl_2	May interfere at levels greater than 6 mg/L. Additional glycine may be able to compensate for this interference.
Chloramines, organic	May interfere.
Flocculating agents	High levels of most flocculating agents can be tolerated. This tolerance is decreased if chlorine is present. See the information about metals in this table. In the presence of 0.6 mg/L Cl_2, $Al(SO_4)_3$ (< 500 mg/L) and $FeCl_2$ (<200 mg/L) may be tolerated.
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$.

Interfering Substance	Interference Levels and Treatments
Iodine, I_2	Interferes at all levels.
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium, oxidized (Cr^{6+})	Oxidized manganese interferes at all levels. Oxidized chromium interferes at levels greater than 2 mg/L. To remove the interferences: **1.** Adjust sample pH to 6–7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result of this test from the original analysis to obtain the correct chlorine dioxide concentration.
Metals	Various metals may interfere by combining with the glycine needed to remove the chlorine interference. Metal interference is limited except when chlorine is present. In the presence of 0.6 mg/L Cl_2, both copper (>10 mg/L) and nickel (>50 mg/L) interfere. Other metals may also interfere, depending on their ability to prevent glycine from reacting with any Cl_2 in the sample. It may be necessary to add more glycine to overcome this interference.
Monochloramine	Causes a gradual drift to higher readings. When read within 1 minute after reagent addition, 3 mg/L monochloramine causes less than a 0.1 mg/L ClO_2 increase in the reading.
Ozone	Interferes at levels greater than 1.5 mg/L.
Peroxides	May interfere.
Extreme sample pH	Adjust to pH 6–7. See *Section 1, pH Interferences, in the DR/800 Procedures Manual.*
Highly buffered samples	Adjust to pH 6–7. *See Section 1, pH Interferences, in the DR/800 Procedures Manual.*

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by Federal RCRA for arsenic (D004).

Summary of Method

Chlorine dioxide reacts with DPD (N,N-diethyl-p-phenylenediamine) Indicator Reagent (to the extent of one-fifth of its total available chlorine content corresponding to reduction of chlorine dioxide to chlorite) to form a pink color. The color intensity is proportional to the ClO_2 in the sample. Chlorine interference is eliminated by adding glycine, which converts free chlorine to chloroaminoacetic acid, but has no effect on chlorine dioxide at the test pH.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required per test	Unit	Cat. No.
Chlorine Dioxide DPD/Glycine Reagent Set (100 tests)			27709-00
Includes one of each:			
DPD Free Chlorine Reagent Powder Pillows, 10 mL	1 pillow	100/pkg	21055-69
Glycine Reagent	4 drops	29 mL	27621-33

REQUIRED REAGENTS (Using AccuVac® Ampuls)

Chlorine Dioxide DPD/Glycine AccuVac® Ampul Reagent Set (25 tests)			27710-00
Includes one of each:			
DPD Free Chlorine Reagent AccuVac® Ampuls	1	25/pkg	25020-25
Glycine Reagent	16 drops	29 mL	27621-33

OPTIONAL REAGENTS

Chlorine Standard Solution, Voluette™ ampule, 50-75 mg/L, 10 mL		16/pkg	14268-10
DPD Free Chlorine Reagent, SwifTest™		250 tests	28023-00
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, deionized		4 L	272-56
Water, sterile, chlorine dioxide-free		500 mL	26415-49

OPTIONAL APPARATUS

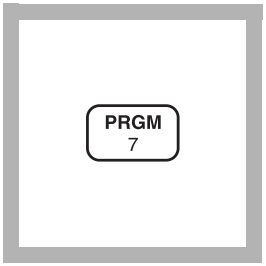
AccuVac® Snapper Kit		each	24052-00
Cylinder, graduated, 25 mL		each	508-40
pH Meter, *sens**ion**™1*, portable, with electrode		each	51700-10
pH Paper, 1 to 11 pH units		5 rolls/pkg	391-33
Pipet, TenSette®, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette® Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette® Pipet		1000/pkg	21856-28
PourRite™ Ampule Breaker		each	24846-00

For Technical Assistance, Price and Ordering
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Marked Dropper Bottle - contact Hach for larger sizes.

CYANURIC ACID (7 to 55 mg/L)

Turbidimetric Method



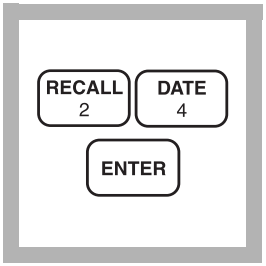
1. Enter the stored program number for cyanuric acid.

Press: **PRGM**

The display will show:

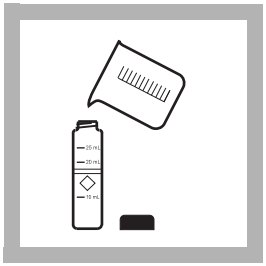
PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



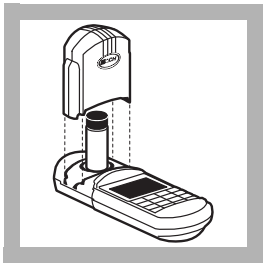
2. Press: **24 ENTER**

The display will show **mg/L, CYACD** and the **ZERO** icon.

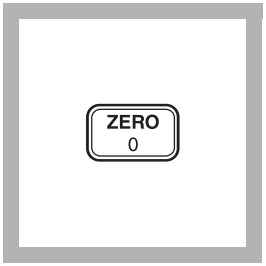


3. Fill a sample cell with 25 mL of sample (the blank).

Note: *Filtering is required for highly turbid samples.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

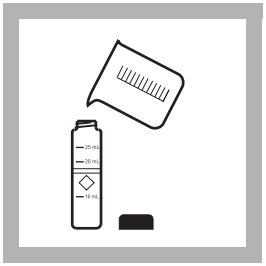


5. Press: **ZERO**

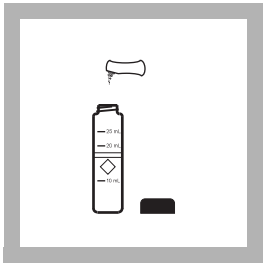
The cursor will move to the right, then the display will show:

0 mg/L CYACD

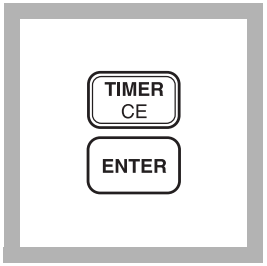
Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



6. Fill another cell with 25 mL of sample.



7. Add the contents of one Cyanuric Acid 2 Reagent Powder Pillow (the prepared sample). Swirl to mix.

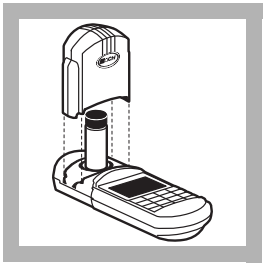


8. Press **TIMER ENTER**

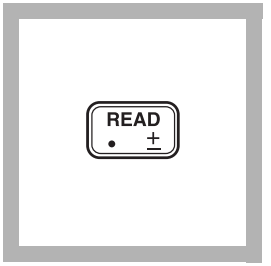
A three-minute reaction period will begin.

Note: *A white turbidity will form if cyanuric acid is present.*

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



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L cyanuric acid will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Note: *Clean sample cells with soap, water and a brush soon after each test to prevent a white film from 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 1000 mL of deionized water to make a 1000 mg/L solution. It takes several hours for the cyanuric acid to dissolve. This solution is stable for several weeks.

b) Dilute 2.00 mL of the 1000 mg/L solution to 100 mL with deionized 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.

Method Performance

Precision

In a single laboratory, using a standard solution of 25.0 mg/L cyanuric acid and two lots of reagent with the instrument, a single

operator obtained a standard deviation of ±1.2 mg/L cyanuric acid.

Estimated Detection Limit

The estimated detection limit for program 24 is 7.0 mg/L cyanuric acid. For more information on the estimated detection limit, see *Section 1*.

Interferences

Turbidity will interfere. Filter turbid samples before running the test.

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. Due to the nature of the precipitation reaction, low levels of cyanuric acid (less than 7 mg/L) are not detected by this method.

REQUIRED REAGENTS AND APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Cyanuric Acid 2 Reagent Powder Pillow	1 pillow	50/pkg	2460-66
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Cyanuric Acid		25 g	7129-24
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

Balance, Acculab UI Series		each	26947-00
Filter Paper, folded 12.5 cm		100/pkg	1894-57
Flask, volumetric, Class A, 100 mL		each	14574-42
Flask, volumetric, Class A, 1000 mL		each	14574-53
Funnel, poly, 65 mm		each	1083-67
Pipet, Bulb		each	14651-00
Pipet, volumetric, Class A, 2.00 mL		each	14515-36

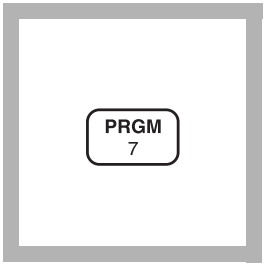
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

HARDNESS (0 to 4.00 mg/L Ca and Mg as $CaCO_3$) For water, wastewater, seawater

Calcium and Magnesium; Calmagite Colorimetric Method



1. Enter the stored program number for magnesium hardness (as $CaCO_3$).

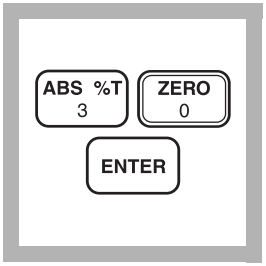
Press: **PRGM**

The display will show:

PRGM ?

Note: *Adjust the pH of stored samples before analysis.*

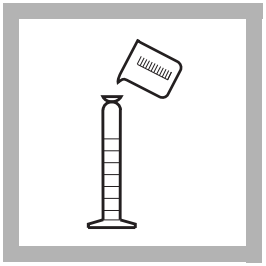
Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **30 ENTER**

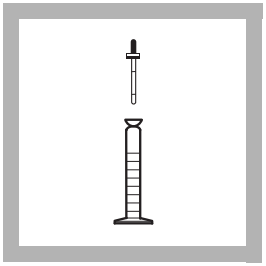
The display will show **mg/L, CaCO3** and the **ZERO** icon**.**

Note: *For alternate forms (Mg, $MgCO_3$), press the* **CONC** *key.*

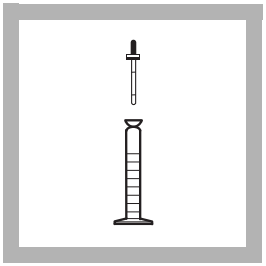


3. Pour 100 mL of sample into a 100-mL graduated mixing cylinder.

Note: *The sample temperature should be 21-29 °C (70-84 °F).*

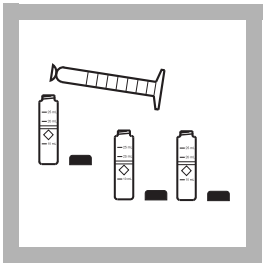


4. Add 1.0 mL of Calcium and Magnesium Indicator Solution using a 1.0-mL measuring dropper. Stopper. Invert several times to mix.



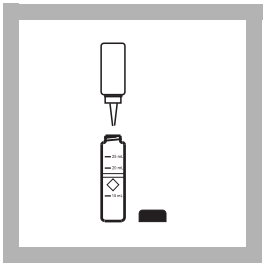
5. Add 1.0 mL of Alkali Solution for Calcium and Magnesium Test using a 1.0-mL measuring dropper. Stopper. Invert several times to mix.

Note: *If the sample turns read after adding Alkali Solution, dilute sample 1:1 and repeat analysis.*

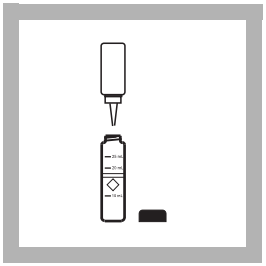


6. Pour 10 mL of the solution into each of three sample cells.

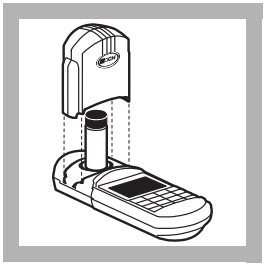
Note: *The test will detect any calcium or magnesium contamination in the mixing cylinder, measuring droppers or sample cells. To test cleanliness, repeat the test multiple times until you obtain consistent results.*



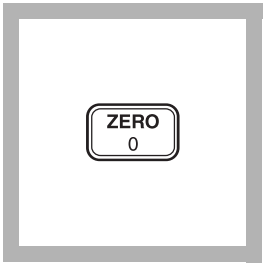
7. Add one drop of 1 M EDTA Solution to one cell (the blank). Swirl to mix.



8. Add one drop of EGTA Solution to another cell (the prepared sample). Swirl to mix.



9. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

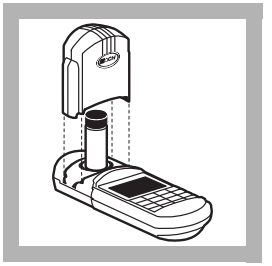


10. Press: **ZERO**

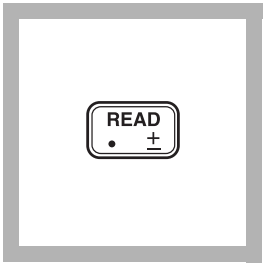
The cursor will move to the right, then the display will show:

0.00 mg/L CaCO3

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*

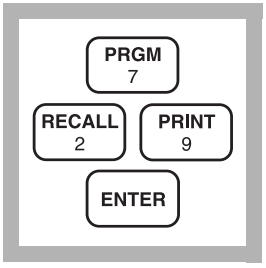


11. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



12. Press: **READ**

The cursor will move to the right, then the result in mg/L magnesium hardness (as $CaCO_3$) will be displayed.



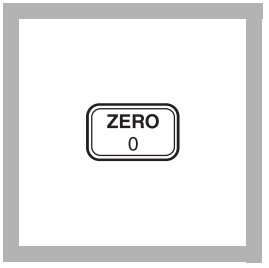
13. Without removing the cell, press:

PRGM 29 ENTER

The display will show:

PRGM ?

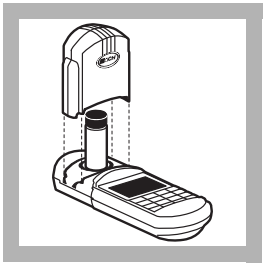
Note: *For alternate forms (Ca) press the* **CONC** *key.*



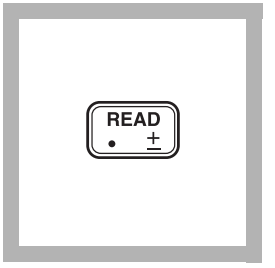
14. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L CaCO3



15. Place the third sample cell into the cell holder.



16. Press: **READ**

The cursor will move to the right, then the result in mg/L calcium hardness (as $CaCO_3$) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Note: *mg/L total hardness = mg/L Ca as $CaCO_3$ + mg/L Mg as $CaCO_3$.*

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. Adjust the sample pH to

between 3 and 8 with 5.0 N Sodium Hydroxide Standard Solution just before analysis. Correct the test results for volume additions; see *Correction for Volume Additions* in *Section 1* for more information.

Accuracy Check

Using a 2.00 mg/L (as $CaCO_3$) standard solution as sample, perform the hardness procedure described above. The results should be 2.00 mg/L calcium (as $CaCO_3$).

Method Performance

Precision

In a single laboratory using a standard solution of 2.00 mg/L Mg as $CaCO_3$ and 1.88 mg/L Ca as $CaCO_3$ with the instrument, a single operator obtained a standard deviation of ± 0.09 mg/L Mg as $CaCO_3$ and ± 0.08 mg/L Ca as $CaCO_3$.

Estimated Detection Limit

The estimated detection limit for program 30 is 0.13 mg/L magnesium hardness and 0.08 mg/L calcium hardness. For more information on the estimated detection limit, see *Section 1*.

Interferences

For the most accurate hardness test result, the test should be rerun on a diluted sample if the calcium is over 1.0 or the magnesium is over
0.25 mg/L as $CaCO_3$. No retesting is needed if either is below those respective concentrations.

The following cause a detectable error in test results.

Interfering Substance	Level at Which Substance Interferes
Cr^{3+}	0.25 mg/L
Cu^{2+}	0.75 mg/L
EDTA, chelated	0.2 mg/L as $CaCO_3$
Fe^{2+}	1.4 mg/L
Fe^{3+}	2.0 mg/L
Mn^{2+}	0.20 mg/L
Zn^{2+}	0.050 mg/L

Traces of EDTA or EGTA remaining in sample cells from previous tests will give erroneous results. Rinse cells thoroughly before use.

Summary of Method

The colorimetric method for measuring hardness supplements the conventional titrimetric method because it can measure very low levels of calcium and magnesium. Also some interfering metals (those listed above) in the titrimetric method are inconsequential in the colorimetric method when diluting the sample to bring it within the range of this test.

The indicator dye, calmagite, forms a purplish-blue color in a strongly alkaline solution and changes to red when it reacts with free calcium or magnesium. Calcium is chelated with EGTA to destroy any red color due to calcium and then the sample is chelated with EDTA to destroy the red color due to both calcium and magnesium. Measuring the red color in the different stages of chelation gives results as the calcium and magnesium hardness concentrations.

REQUIRED REAGENTS

	Cat. No.
Hardness Reagent Set (100 Tests)	23199-00
Includes: (1) 22417-32, (1) 22418-32, (1) 22419-26, (1) 22297-26	

Description	Quantity Required Per Test	Unit	Cat. No.
Alkali Solution for Calcium and Magnesium Test	1 mL	100 mL MDB	22417-32
Calcium and Magnesium Indicator Solution	1 mL	100 mL MDB	22418-32
EDTA Solution, 1 M	1 drop	50 mL	22419-26
EGTA Solution	1 drop	50 mL	22297-26

REQUIRED APPARATUS

Cylinder, 100-mL mixing	1	each	1896-42
Dropper, measuring, 0.5 and 1.0 mL	2	20/pkg	21247-20
Sample Cell, 10-20-25 mL, w/cap	3	6/pkg	24019-06

OPTIONAL REAGENTS

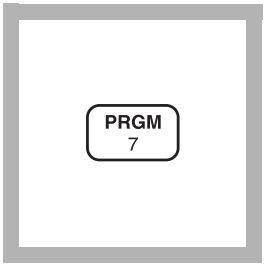
Calcium Standard Solution, 2.0 mg/L as $CaCO_3$	946 mL	20581-16
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Sodium Hydroxide Standard Solution 5.0 N	100 mL MDB	2450-32

OPTIONAL APPARATUS

pH Meter, *sens**ion***™***1**, portable, with electrode	each	51700-10
Thermometer, –20 to 110 °C	each	26357-02

1,10 Phenanthroline Method* (Powder Pillows or AccuVac Ampuls)

Using Powder Pillows



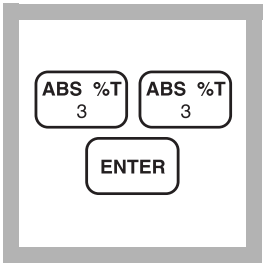
1. Enter the stored program number for Ferrous iron (Fe^{2+})-powder pillows.

Press: **PRGM**

The display will show:

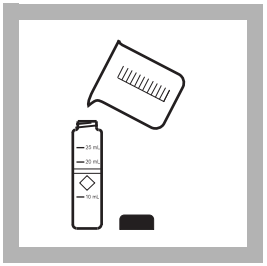
PRGM ?

Note: *Analyze samples as soon as possible to prevent oxidation of ferrous iron to ferric iron, which is not determined.*

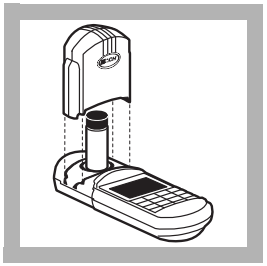


2. Press: **33 ENTER**

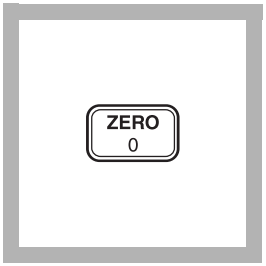
The display will show **mg/L, Fe** and the **ZERO** icon.



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



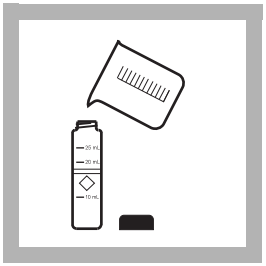
4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



5. Press: **ZERO**

The cursor will move to the right, then the display will show:

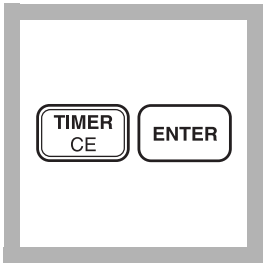
0.00 mg/L Fe



6. Fill another sample cell with 25 mL of sample.

7. Add the contents of one Ferrous Iron Reagent Powder Pillow to the sample cell (the prepared sample). Cap and invert to mix.

Note: *Undissolved powder does not affect accuracy.*



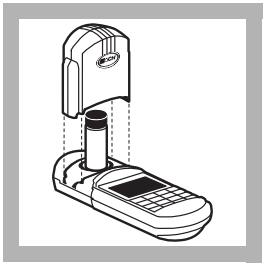
8. Press:

TIMER ENTER

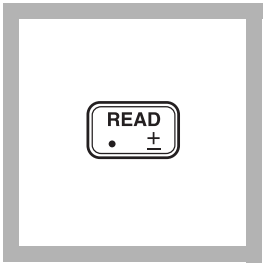
A three-minute reaction period will begin.

Note: *An orange color will form if ferrous iron is present.*

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



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

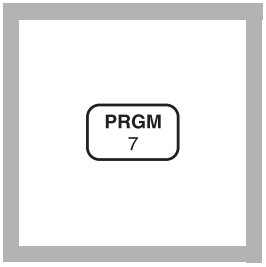


10. Press: **READ**

The cursor will move to the right, then the result in mg/L ferrous iron will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Using AccuVac Ampuls



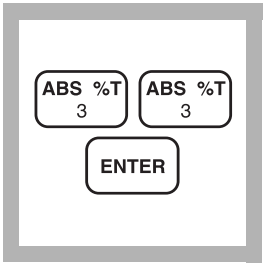
1. Enter the stored program number for ferrous iron (Fe^{2+}) AccuVac ampuls.

Press: **PRGM**

The display will show:

PRGM ?

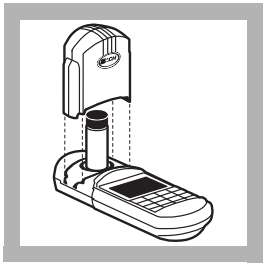
Note: *Analyze samples as soon as possible to prevent air oxidation of ferrous iron to ferric, which is not determined.*



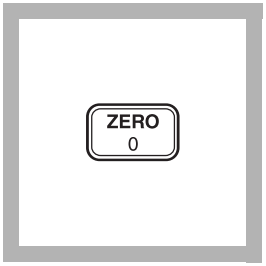
2. Press: **33 ENTER**

The display will show **mg/L, Fe** and the **ZERO** icon.

3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.



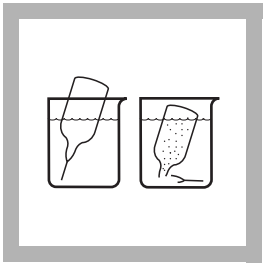
4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



5. Press: **ZERO**

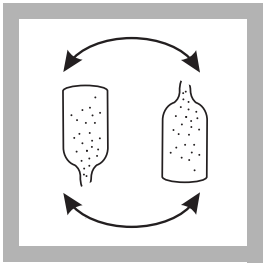
The cursor will move to the right, then the display will show:

0.00 mg/L Fe



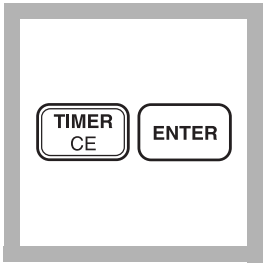
6. Fill a Ferrous Iron AccuVac Ampul with sample.

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



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

Note: *Undissolved powder does not affect accuracy.*

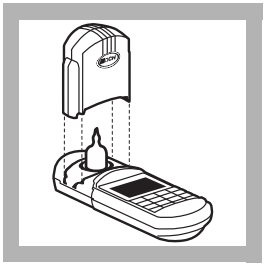


8. Press:

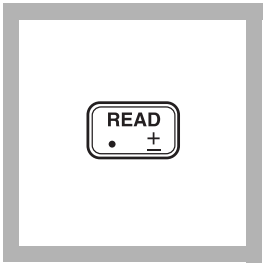
TIMER ENTER

A three-minute reaction period will begin.

Note: *An orange color will form if ferrous iron is present.*



9. Place the AccuVac ampul into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L ferrous iron will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Sampling and Storage

Ferrous iron must be analyzed immediately and cannot be stored. Analyze samples as soon as possible to prevent oxidation of ferrous iron to ferric iron, which is not measured.

Accuracy Check

Standard Solution Method

Prepare a ferrous iron stock solution (100 mg/L Fe^{2+}) by dissolving 0.7022 grams of ferrous ammonium sulfate, hexahydrate, in deionized water. Dilute to 1 liter. Prepare immediately before use. Dilute 1.00 mL of this solution to 100 mL with deionized water to make a 1.00 mg/L standard solution. Prepare immediately before use.

Run the test using the 1.00 mg/L Fe^{2+} Standard Solution by following either the powder pillow or AccuVac procedure. Results should be between 0.90 mg/L and 1.10 mg/L Fe^{2+}.

Method Performance

Precision

In a single laboratory using an iron standard solution of 2.00 mg/L Fe^{2+} and two representative lots of powder pillow reagents with the instrument, a single operator obtained a standard deviation of ±0.017 mg/L Fe^{2+}.

In a single laboratory using a standard solution of 2.00 mg/L Fe^{2+} and two representative lots of AccuVac ampuls with the instrument, a single operator obtained a standard deviation of ±0.009 mg/L Fe^{2+}.

Estimated Detection Limit

The estimated detection limit for program 33 (powder pillows and AccuVac Ampuls) is 0.03 mg/L Fe. For more information on the estimated detection limit, see *Section 1*.

Summary of Method

The 1,10-phenanthroline indicator in Ferrous Iron Reagent reacts with ferrous iron in the sample to form an orange color in proportion to the iron concentration. Ferric iron does not react. The ferric iron (Fe^{3+}) concentration can be determined by subtracting the ferrous iron concentration from the results of a total iron test.

REQUIRED REAGENTS & APPARATUS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Units	Cat. No.
Ferrous Iron Reagent Powder Pillows	1 pillow	100/pkg	1037-69
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

REQUIRED REAGENTS & APPARATUS (USING ACCUVAC AMPULS)

Ferrous Iron Reagent AccuVac Ampuls	1 ampul	25/pkg	25140-25
Beaker, 50 mL	1	each	500-41H

OPTIONAL REAGENTS

Ferrous Ammonium Sulfate, hexahydrate, ACS		113 g	11256-14
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit		each	24052-00
Balance, analytical, 115 V, 0.1 mg		each	28014-01
Balance, analytical, 230 V, 0.1 mg		each	28014-02
Clippers, for opening powder pillows		each	968-00
Flask, volumetric, 100 mL, Class A		each	14574-42
Flask, volumetric, 1000 mL, Class A		each	14574-53
Pipet, volumetric, Class A, 1.00 mL		each	14515-35
Pipet Filler, safety bulb		each	14651-00
Weighing Boat, 67/46 mm, 8.9 cm square		500/pkg	21790-00

For Technical Assistance, Price and Ordering

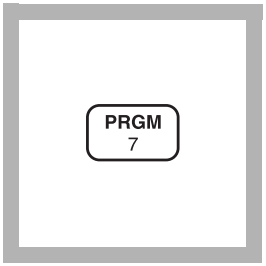
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

IRON, TOTAL (0 to 3.00 mg/L)

FerroVer Method (Powder Pillows or AccuVac Ampuls)

USEPA approved for reporting wastewater analysis (digestion is required; see Section 2*)



1. Enter the stored program number for iron (Fe) powder pillows.

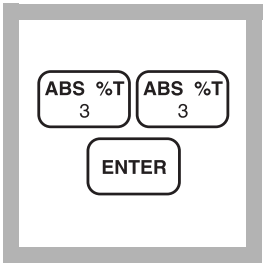
Press: **PRGM**

The display will show:

PRGM ?

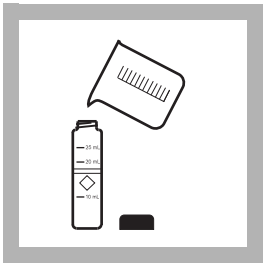
Note: *Determination of total iron requires a digestion prior to analysis (see Section 2).*

Note: *Adjust pH of stored samples before analysis.*



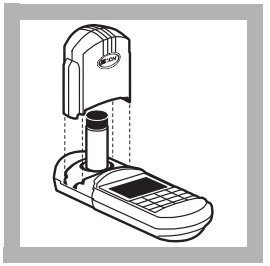
2. Press: **33 ENTER**

The display will show **mg/L, Fe** and the **ZERO** icon**.**

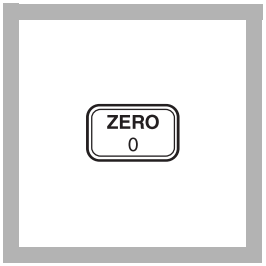


3. Fill a clean sample cell with 10 mL of sample (the blank).

Note: *For turbid samples, treat the blank with one 0.1-gram scoop of RoVer Rust Remover. Swirl to mix.*



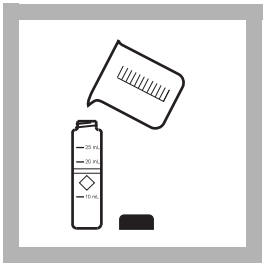
4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



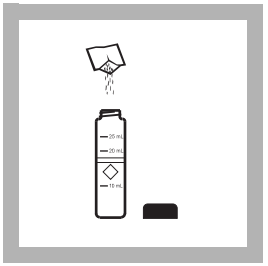
5. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L Fe

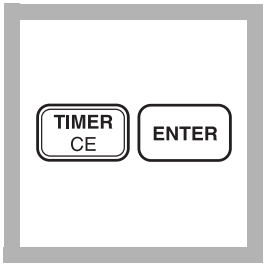


6. Fill another sample cell with 10 mL of sample.



7. Add the contents of one FerroVer Iron Reagent Powder Pillow to the sample cell (the prepared sample). Cap and invert to dissolve the reagent powder.

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



8. Press:

TIMER ENTER

A three-minute reaction period will begin.

Note: *An orange color will form if iron is present.*

Note: *Samples containing visible rust should be allowed to react at least five minutes.*

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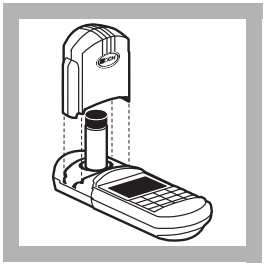
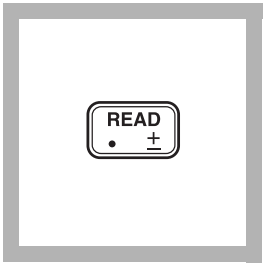
* *Federal Register*, 45 (126) 43459 (June 27, 1980). See also 40 CFR, part 136.3, Table IB.



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

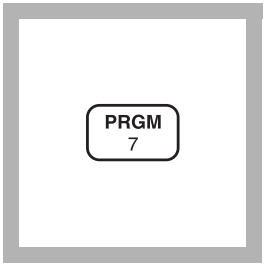


10. Press: **READ**

The cursor will move to the right, then the result in mg/L iron (Fe) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Using AccuVac Ampuls



1. Enter the stored program number for iron (Fe), AccuVac ampuls.

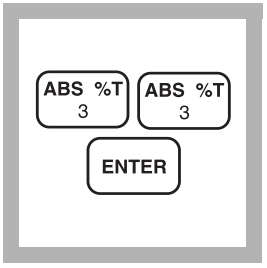
Press: **PRGM**

The display will show:

PRGM ?

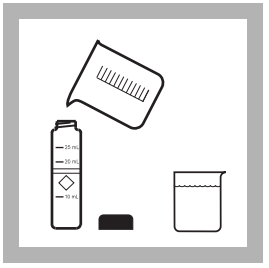
Note: *Adjust pH of stored samples before analysis.*

Note: *Determination of total iron requires a digestion prior to analysis (see Section 2).*



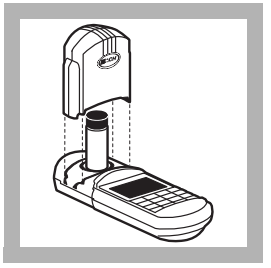
2. Press: **33 ENTER**

The display will show **mg/L, Fe** and the **ZERO** icon**.**

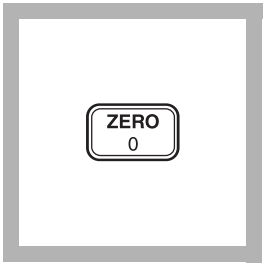


3. Fill a sample cell (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

Note: *For turbid samples, treat the blank with one 0.1 g scoop of RoVer Rust Remover. Swirl to mix.*



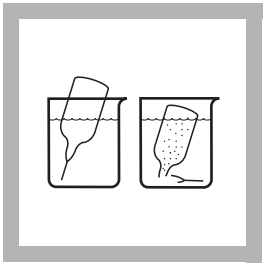
4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



5. Press: **ZERO**

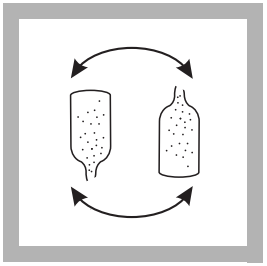
The cursor will move to the right, then the display will show:

0.00 mg/L Fe



6. Fill a FerroVer AccuVac Ampul with sample.

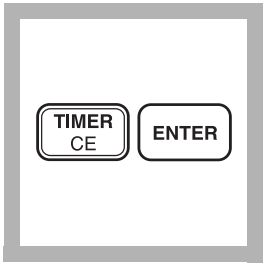
Note: *Keep the tip immersed while the ampul fills completely.*



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

Note: *An orange color will form if iron is present.*

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

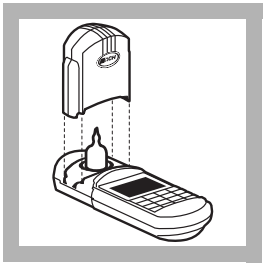


8. Press:

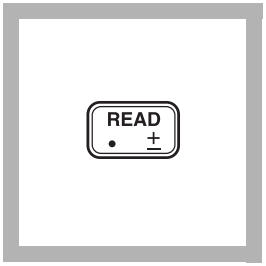
TIMER ENTER

A three-minute reaction period will begin.

Note: *Samples containing visible rust should be allowed to react at least five minutes.*



9. Place the AccuVac ampul into the cell holder. Tightly cover the ampul with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L iron (Fe) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in acid-cleaned glass or plastic containers. No acid addition is necessary if analyzing the sample immediately. To preserve samples, 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. Adjust the pH to between 3 and 5 with 5.0 N Sodium Hydroxide Standard Solution before analysis. Correct the test result for volume additions; see *Correcting for Volume Additions* in *Section 1* for more information. If only dissolved iron is to be determined, filter the sample before adding the acid.

Accuracy Check

Standard Additions Method

a) Snap the neck off a 50 mg/L Iron PourRite Ampule Standard Solution.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard, respectively, to three 25-mL samples and mix thoroughly.

c) For analysis using AccuVac Ampuls, transfer solutions to dry, clean 50-mL beakers to facilitate filling of the ampuls. For analysis with powder pillows, transfer only 10 mL of solution to the 10-mL sample cells.

d) Analyze each standard addition sample as described above. The iron concentration should increase 0.2 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* in *Section 1* for troubleshooting information.

Standard Solution Method

Prepare a 1.0-mg/L iron standard by diluting 1.00 mL of Iron Standard Solution, 100 mg/L Fe, to 100 mL with deionized water. Or, dilute 1.00 mL of an Iron PourRite Ampule Standard Solution (50 mg/L) to 50 mL in a volumetric flask. Prepare this solution daily.

Run the test following the procedure for powder pillows or AccuVac Ampuls. Results should be between 0.90 mg/L and 1.10 mg/L Fe.

Method Performance

Precision

In a single laboratory, using a standard solution of 2.00 mg/L Fe and two representative lots of powder pillow reagents with the instrument, a single operator obtained a standard deviation of ±0.017 mg/L.

In a single laboratory, using a standard solution of 2.00 mg/L Fe and two representative lots of AccuVac ampuls with the instrument, a single operator obtained a standard deviation of ±0.009 mg/L Fe.

Estimated Detection Limit (EDL)

The EDL for program 33 is 0.03 mg/L Fe. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substances and Suggested Treatments

Interfering Substance	Interference Level and Treatment
Calcium, Ca^{2+}	No effect at less than 10,000 mg/L as $CaCO_3$
Chloride, Cl^-	No effect at less than 185,000 mg/L.
Copper, Cu^{2+}	No effect. Masking agent is contained in FerroVer Iron Reagent.
High Iron Levels	Inhibits color development. Dilute sample and retest to verify results.
Iron Oxide	Requires mild, vigorous or Digesdahl digestion (see Section 2). After digestion, adjust sample to pH 3-5 with sodium hydroxide, then analyze.
Magnesium	No effect at 100,000 mg/L as $CaCO_3$.
Molybdate, Molybdenum	No effect at 25 mg/L as Mo.
High Sulfide Levels, S^{2-}	**1.** Treat in fume hood or well-ventilated area. Add 5 mL HCl to 100 mL sample in a 250-mL Erlenmeyer flask. Boil 20 minutes. **2.** Cool. Adjust pH to 3-5 with NaOH. Re-adjust volume to 100 mL with deionized water. **3.** Analyze.

Interfering Substance	Interference Level and Treatment
Turbidity	**1.** Add 0.1 g scoop of RoVer Rust Remover to the blank in Step 3. Swirl to mix. **2.** Zero the instrument with this blank. **3.** If sample remains turbid, add three 0.2 g scoops of RoVer to a 75-mL sample. Let stand 5 minutes. **4.** Filter through a glass filter or centrifuge. **5.** Use filtered sample in Steps 3 and 6.
Sample pH (extreme)	Adjust pH to 3-5. See *Interferences* in *Section 1*.
Highly Buffered Samples	Adjust pH to 3-5. See *Interferences* in *Section 1*.

Summary of Method

FerroVer Iron Reagent reacts with all soluble iron and most insoluble forms of iron in the sample to produce soluble ferrous iron. This reacts with 1,10-phenanthroline indicator in the reagent to form an orange color in proportion to the iron concentration.

REQUIRED REAGENTS & APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat No.
FerroVer Iron Reagent Powder Pillows	1 pillow	100/pkg	21057-69
Sample cell, 10-20-25 mL, with screw cap	1	6/pkg	24019-06

REQUIRED REAGENTS & APPARATUS (Using AccuVac Ampuls)

FerroVer Iron Reagent AccuVac Ampuls	1 ampul	25/pkg	25070-25
Beaker, 50 mL	1	each	500-41H

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Ammonium Hydroxide, ACS	500 mL	106-49
Drinking Water Standard, Metals, LR (Cu, Fe, Mn)	500 mL	28337-49
Drinking Water Standard, Metals, HR (Cu, Fe, Mn)	500 mL	28336-49
Hydrochloric Acid Standard Solution, 6 N	500 mL	884-49
Hydrochloric Acid, ACS	500 mL	134-49
Iron Standard Solution, 100 mg/L	100 mL	14175-42
Iron Ampule Standard, 50 mg/L	20/pkg	14254-20
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
RoVer Rust Remover	454 g	300-01
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each		24052-00
Ampule Breaker, PourRite Ampules	each		24846-00
Clippers, Shears $7^{1}/_{4}$ "	each		23694-00
Cylinder, graduated, poly, 25 mL	each		1081-40
Cylinder, graduated, poly, 100 mL	each		1081-42
Digesdahl Digestion Apparatus, 115 V	each		23130-20
Digesdahl Digestion Apparatus, 230 V	each		23130-21
Filter Discs, glass, 47 mm	100/pkg		2530-00
Filter Holder, membrane	each		2340-00
Filter Pump	each		2131-00
Flask, Erlenmeyer, 250 mL	each		505-46
Flask, filtering, 500 mL	each		546-49
Flask, volumetric, Class A, 50 mL	each		14574-41
Flask, volumetric, Class A, 100 mL	each		14574-42
Hot Plate, 4" diameter, 120 VAC	each		12067-01
Hot Plate, 4" diameter, 240 VAC	each		12067-02
pH Meter, *sens**ion***™***1***, portable, with electrode	each		51700-10
pH Indicator Paper, 1 to 11 pH	each		391-33
Pipet Filler, safety bulb	each		14651-00
Pipet, serological, 2 mL	each		532-36
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 Tips, for 19700-01 TenSette Pipet	1000/pkg		21856-28
Pipet, volumetric, Class A, 1.00 mL	each		14515-35
Spoon, measuring, 0.1 g	each		511-00

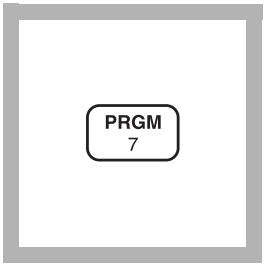
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

MANGANESE, High Range (0 to 20.0 mg/L)

Periodate Oxidation Method* USEPA approved for reporting wastewater analysis (digestion is required; see Section 2)**

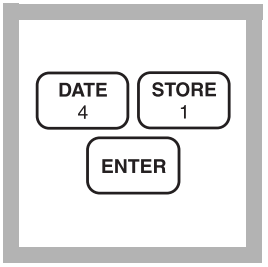


1. Enter the stored program number for manganese, periodate oxidation method.

Press: **PRGM**

The display will show:

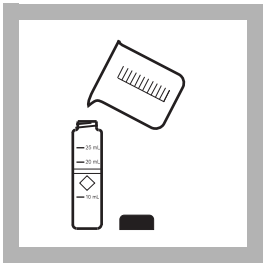
PRGM ?



2. Press: **41 ENTER**

The display will show **mg/L, Mn** and the **ZERO** icon**.**

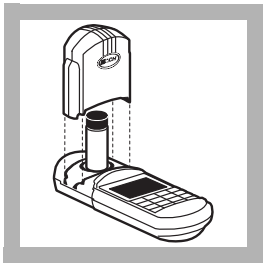
Note: *For alternate forms ($KMnO_4$, MnO_4), press the* **CONC** *key.*



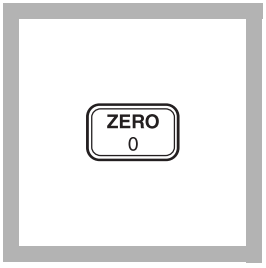
3. Fill a sample cell with 10 mL of sample (the blank).

Note: *For total manganese determination perform a digestion (see Section 2).*

Note: *Adjust the pH of stored samples before analysis.*



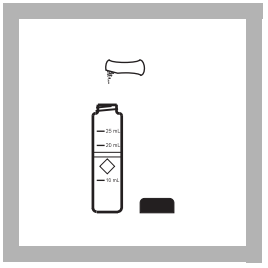
4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



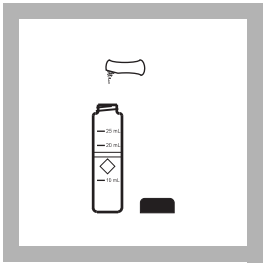
5. Press: **ZERO**

The cursor will move to the right, then the display will show:

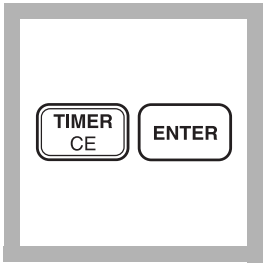
0.0 mg/L Mn



6. Remove the cell from the instrument. Add the contents of one Buffer Powder Pillow, citrate type, to the cell. Cap the cell and invert until the powder is dissolved. Remove cap.



7. Add the contents of one Sodium Periodate Powder Pillow to the sample cell (the prepared sample). Cap the sample cell. Invert for 10 seconds to mix.



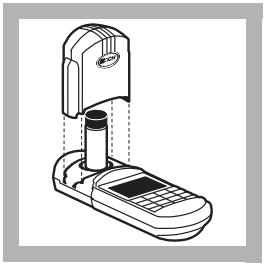
8. Press:**TIMER ENTER**

A two-minute reaction period will begin.

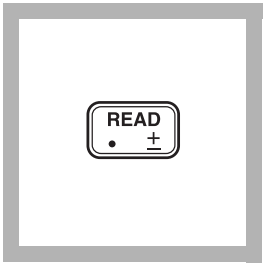
Note: *A violet color will form if manganese is present.*

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

** *Federal Register,* 44 (116) 34193 (June 14, 1979).



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L manganese will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in acid-washed plastic bottles. Manganese may be lost by adsorption to glass container walls. Adjust the pH to less than 2 with nitric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature. Adjust the pH to 4 to 5 with 5.0 N sodium hydroxide before analysis. Do not exceed pH 5, as manganese may be lost as a precipitate. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section 1* for more information. If only dissolved Mn is to be determined, filter before acid addition.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Manganese Voluette Ampule Standard Solution, 250 mg/L Mn.

b) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard, respectively, to the three 25-mL water samples. Swirl to mix.

c) Transfer only 10 mL of each solution to the 10-mL sample cells.

d) Analyze each standard addition sample as described in the procedure. The manganese concentration should increase 1.0 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* in *Section 1* for troubleshooting information.

Standard Solution Method

Prepare a 5.0 mg/L manganese standard solution by pipetting (use a TenSette or Class A volumetric pipet) 5.00 mL of Manganese Standard Solution, 1000 mg/L Mn, into a 1000-mL volumetric flask. Dilute to the mark with deionized water. Or, prepare this standard by diluting 1.00 mL of a High Range Manganese Standard Voluette Ampule, 250 mg/L, to 50 mL. Prepare these solutions daily. Use these solutions as the sample in the procedure.

Method Performance

Precision

In a single laboratory, using a standard solution of 10.00 mg/L Mn and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.18 mg/L Mn.

Estimated Detection Limit

The estimated detection limit for program 41 is 0.2 mg/L Mn. For more information on the estimated detection limit, see *Section 1*.

Interferences

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

Calcium	700 mg/L
Chloride	70,000 mg/L
Iron	5 mg/L
Magnesium	100,000 mg/L

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section 1*.

Summary of Method

Manganese in the sample is oxidized to the purple permanganate state by sodium periodate, after buffering the sample with citrate. The purple color is directly proportional to the manganese concentration.

REQUIRED REAGENTS

	Cat. No.
High Range Manganese Reagent Set (100 tests) 10 mL	24300-00
Includes: (1) 21076-69, (1) 21077-69	

Description	Quantity Required Per Test	Unit	Cat. No.
Buffer Powder Pillows, citrate type for Manganese	1 pillow	100/pkg	21076-69
Sodium Periodate Powder Pillows for Manganese	1 pillow	100/pkg	21077-69

REQUIRED APPARATUS

Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Drinking Water Standard, Metals, HR (Cu, Fe, Mn)	500 mL	28336-49
Hydrochloric Acid, 6 N	500 mL	884-49
Manganese Standard Solution, 1000 mg/L Mn	100 mL	12791-42
Manganese Standard Solution, Voluette ampule, High Range, 250 mg/L Mn, 10 mL	16/pkg	14258-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution 1:1	500 mL	2540-49
Sodium Hydroxide Solution, 5.0 N	100 mL MDB	2450-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Flask, Erlenmeyer, 250 mL	each	505-46
Flask, volumetric, Class A, 50 mL	each	14574-41
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, *sens**ion***™*1*, portable, with electrode	each	51700-10
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet, TenSette, 1.0 to 10.0 mL	each	19700-10
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96Pipet
Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Pipet Tips, for 19700-10 TenSette Pipet	50/pkg	21997-96
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet Filler, safety bulb	each	14651-00

For Technical Assistance, Price and Ordering

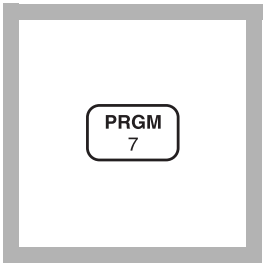
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

NITRATE, High Range (0 to 30.0 mg/L NO_3^--N) For water, wastewater, and seawater*

Cadmium Reduction Method (Using Powder Pillows or AccuVac Ampuls)

Using Powder Pillows



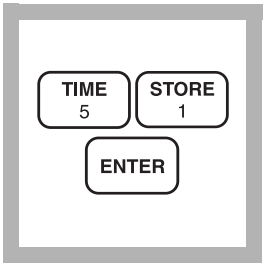
1. Enter the stored program number for high range nitrate nitrogen (NO_3^-–N) powder pillows.

Press: **PRGM**

The display will show:

PRGM ?

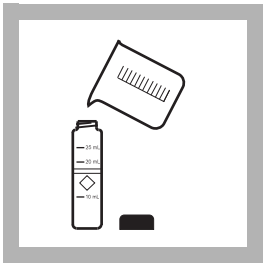
Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **51 ENTER**

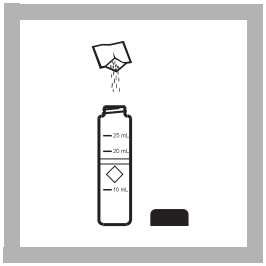
The display will show **mg/L, NO3-N** and the **ZERO** icon**.**

Note: *For alternate forms (NO_3), press the* **CONC** *key.*



3. Fill a sample cell with 10 mL of sample.

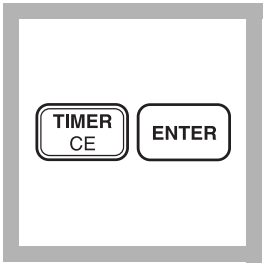
Note: *Adjust the pH of stored samples before analysis.*



4. Add the contents of one NitraVer 5 Nitrate Reagent Powder Pillow to the sample cell (the prepared sample). Cap the sample cell.

Note: *It is important to remove all of the powder from the foil pillow. Tap the pillow until no more powder pours out.*

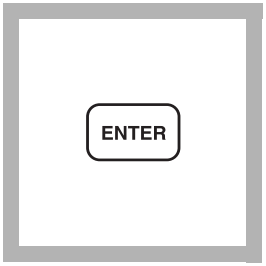
* Seawater requires a manual calibration; see Interferences.



5. Press:
TIMER ENTER

A one-minute reaction period will begin. Shake the sample cell vigorously until the timer beeps.

Note: *It is important to shake the cell vigorously. Shaking time and technique influence color development. For most accurate results, do successive tests on a standard solution and adjust the shaking time to obtain the correct result.*



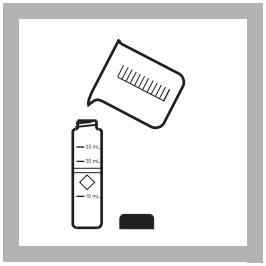
6. After the timer beeps, the display will show:
5:00 TIMER 2

Press: **ENTER**

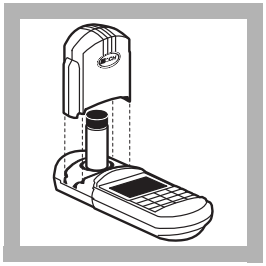
A five-minute reaction period will begin.

Note: *A deposit will remain after the reagent dissolves and will not affect test results.*

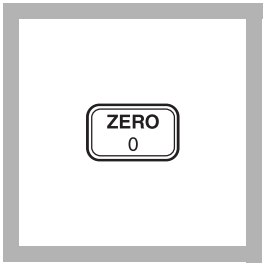
Note: *An amber color will develop if nitrate nitrogen is present.*



7. Fill another cell with 10 mL of sample (the blank). Wipe off any fingerprints or liquid.



8. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

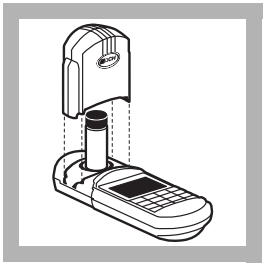


9. When the timer beeps, press **ZERO.**

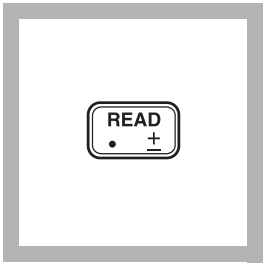
The cursor will move to the right, then the display will show:

0.0 mg/L NO3-N

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



10. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



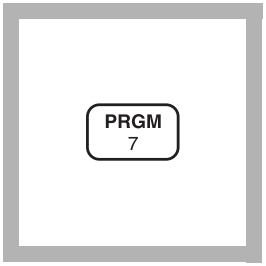
11. Press: **READ**

The cursor will move to the right, then the result in mg/L NO_3-N (or alternate form) will be displayed.

Note: *Use of the Standard Adjust feature for each new lot of reagent is highly recommended. See* Accuracy Check.

Note: *Rinse the sample cell immediately after use to remove all cadmium particles. Save the spent sample for proper hazardous waste disposal for cadmium.*

Using AccuVac Ampuls



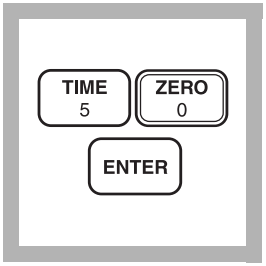
1. Enter the stored program number for high range nitrate nitrogen (NO_3^-–N) AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

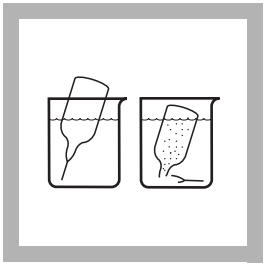
Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **50 ENTER**

The display will show **mg/L, NO3-N** and the **ZERO** icon.

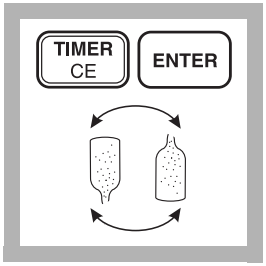
Note: *For alternate forms (NO_3), press the* **CONC** *key.*



3. Collect at least 40 mL of sample in a 50-mL beaker. Fill a NitraVer 5 Nitrate AccuVac Ampul with sample. Place a stopper over the tip of the ampul.

Note: *Keep the tip immersed while the ampul fills. The ampul will not fill completely.*

Note: *Adjust the pH of stored samples before analysis.*

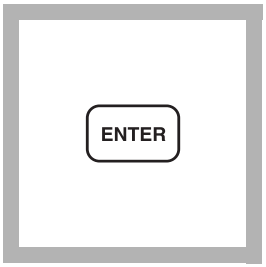


4. Press:

TIMER ENTER

A one-minute mixing period will begin. Invert the ampul repeatedly back and forth until the timer beeps. Wipe off any liquid or fingerprints.

Note: *Mixing time and technique influence color development. For most accurate results, do successive tests on a standard solution and adjust the mixing time to obtain the correct result.*



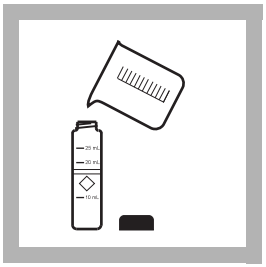
5. The display will show: **5:00 TIMER 2**

Press: **ENTER**

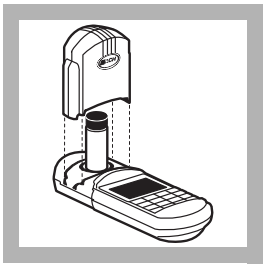
A five-minute reaction period will begin.

Note: *A deposit will remain after the reagent dissolves and will not affect results.*

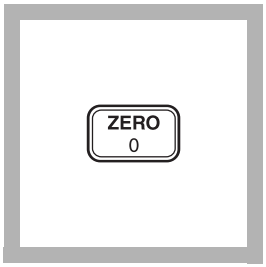
Note: *An amber color will develop if nitrate nitrogen is present.*



6. Fill a sample cell with at least 10 mL of sample (the blank).



7. When the timer beeps, place the blank in the cell holder. Tightly cover the sample cell with the instrument cap.

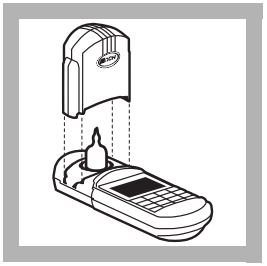


8. Press: **ZERO**

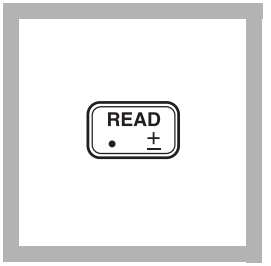
The cursor will move to the right, then the display will show:

0.0 mg/L NO3-N

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



9. Place the AccuVac Ampul into the cell holder. Tightly cover the ampul with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L NO_3-N (or alternate form) will be displayed.

Note: *Use of the Standard Adjust feature for each new lot of reagent is highly recommended. See* Accuracy Check.

Note: *See Pollution Prevention and Waste Management for proper disposal of cadmium.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before running the test. For longer storage periods, adjust sample pH to 2 or less with sulfuric acid, ACS (about 2 mL per liter). Sample refrigeration is still required.

Before testing the stored sample, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution.

Do not use mercury compounds as preservatives.

Correct the test result for volume additions; see *Correction for Volume Additions* (*Section 1*) for more information.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL mixing cylinders with 25 mL of sample.

b) Snap the neck off a Nitrate Nitrogen Ampule Standard, 500 mg/L nitrate nitrogen.

c) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of Nitrate Nitrogen Standard Solution to the three samples. Stopper and mix thoroughly.

d) For AccuVac analysis, transfer the solutions to clean, dry 50-mL beakers. For analysis with powder pillows, transfer only 10 mL of solution to clean, dry sample cells.

e) Analyze each sample as described above. The nitrate nitrogen (NO_3^--N) concentration should increase 2.0 mg/L for each 0.1 mL of standard added.

f) If these increases do not occur, see *Standard Additions* (*Section 1*) for more information.

Standard Solution Method

Use a Hach Nitrate-Nitrogen Standard Solution, 10.0 mg/L NO_3^--N, listed under Optional Reagents as the sample and perform the procedure as described above.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 10.0-mg/L standard solution, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **10.0** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the curve adjustment. See *Section 1, Standard Curve Adjustmen*t for more information. If you are using a reagent blank correction, the blank correction should be entered before the Standard Adjust value is entered.

Method Performance

Precision

In a single laboratory using standard solutions of 25.0 mg/L nitrate nitrogen (NO_3^--N) and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of $\pm$0.3 mg/L nitrate nitrogen for program #50 and ±1.7 mg/L nitrate nitrogen for program # 51.

Estimated Detection Limit

The estimated detection limit for program 50 is 0.5 mg/L NO_3^--N and 0.8 mg/L NO_3^--N for program 51. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Chloride	Chloride concentrations above 100 mg/L will cause low results. The test may be used at high chloride concentrations (seawater) but a calibration must be done using standards spiked to the same chloride concentration.
Ferric iron	All levels
Nitrite	All levels Compensate for nitrite interference as follows: Add 30-g/L Bromine Water dropwise to the sample in Step 3 until a yellow color remains. Add one drop of 30-g/L Phenol Solution to destroy the color. Proceed with Step 4. Report the results as total nitrate and nitrite.
pH	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.
Strong oxidizing and reducing substances	Interfere at all levels.

Summary Of Method

Cadmium metal reduces nitrates present in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt which couples to gentisic acid to form an amber-colored product.

Pollution Prevention and Waste Management

NitraVer 5 contains cadmium metal. Both samples and reagent blanks will contain cadmium (D006) at a concentration regulated as hazardous wastes by the Federal RCRA. Do not pour these solutions down the drain. See *Section 3* for more information on proper disposal of these materials.

REQUIRED REAGENTS & APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
NitraVer 5 Nitrate Reagent Powder Pillows	1 pillow	100/pkg	21061-69
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

REQUIRED REAGENTS (Using AccuVac Ampuls)

NitraVer 5 Nitrate Reagent AccuVac Ampul	1 ampul	25/pkg	25110-25

REQUIRED APPARATUS (Using AccuVac Ampuls)

Beaker, 50 mL	1	each	500-41H
Stopper	1	6/pkg	1731-06

OPTIONAL REAGENTS

Bromine Water 30 g/L		29 mL*	2211-20
Nitrate Nitrogen Standard Solution, 10.0 mg/L as (NO_3^--N)		500 mL	307-49
Nitrate Nitrogen Standard Solution, 1000 mg/L as (NO_3^--N)		500 mL	12792-49
Nitrate Nitrogen Standard Solution, PourRite ampule, 500 mg/L as NO_3^--N, 2 mL		20/pkg	14260-20
Phenol Solution		29 mL	2112-20
Sodium Hydroxide Standard Solution, 5.0 N		50 mL*	2450-26
Sulfuric Acid, ACS		500 mL*	979-49
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit		each	24052-00
Cylinder, graduated, mixing, 25 mL		each	1896-40
Dropper, for 29-mL bottle		each	2258-00
pH Indicator Paper, 1 to 11 pH		5 rolls/pkg	391-33
pH Meter, *sens**ion***™*1*, portable, with electrode		each	51700-10
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 Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
PourRite Ampule Breaker		each	24846-00
Thermometer, –20 to 110 °C, non-mercury		each	26357-02

For Technical Assistance, Price and Ordering

In the U.S.A. call 800-227-4224

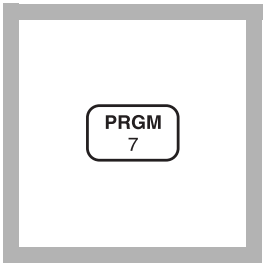
Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Contact Hach for larger sizes.

NITRATE, Low Range (0 to 0.50 mg/L NO_3^--N)

For water, wastewater and seawater*

Cadmium Reduction Method



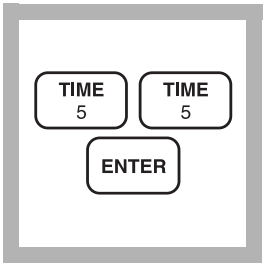
1. Enter the stored program number for low range nitrate nitrogen (NO_3^--N).

Press: **PRGM**

The display will show:

PRGM ?

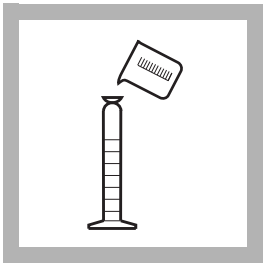
Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **55 ENTER**

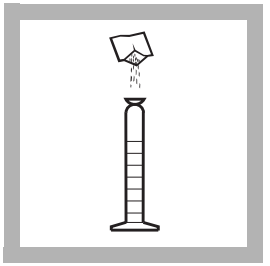
The display will show **mg/L, NO3-N** and the **ZERO** icon**.**

Note: *For alternate forms (NO_3), press the* **CONC** *key.*



3. Fill a 25-mL graduated mixing cylinder to the 15-mL mark with sample.

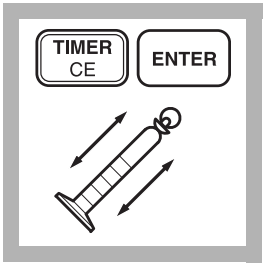
Note: *Adjust the pH of stored samples before analysis.*



4. Add the contents of one NitraVer 6 Nitrate Reagent Powder Pillow to the cylinder. Stopper.

Note: *It is necessary to remove* ***all*** *the powder from the foil pillow. Tap the pillow until no more powder pours out. Be sure to remove powder from the corners of the pillow.*

* Seawater requires a manual calibration; see Interferences.

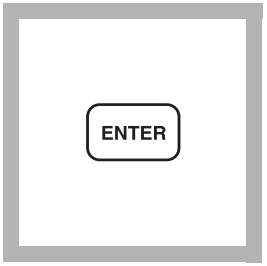


5. Press:

TIMER ENTER

A 3-minute reaction period will begin. Shake the cylinder vigorously throughout this three minute period.

Note: *Shaking time and technique influence color development. For most accurate results, analyze a standard solution several times and adjust the shaking time to obtain the correct result.*

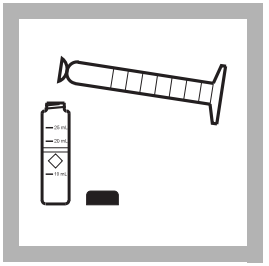


6. When the timer beeps, the display will show: **2:00 TIMER 2**

Press: **ENTER**

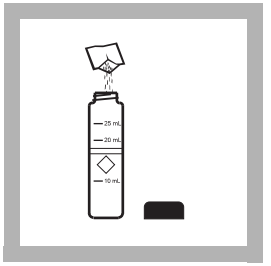
A 2-minute reaction period will begin.

Note: *A deposit will remain after the powder dissolves and will not affect results.*



7. When the timer beeps, pour 10 mL of the sample into a sample cell.

Note: *Do not transfer any cadmium particles.*



8. Add the contents of one NitriVer 3 Nitrite Reagent Powder Pillow to the sample cell (the prepared sample). Cap the cell and shake gently for 30 seconds.

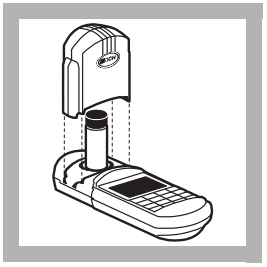
Note: *A pink color will form if nitrate is present.*

9. The display will show: **15:00 TIMER 3**

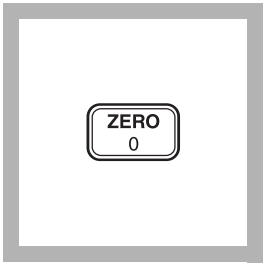
Press: **ENTER**

A 15-minute reaction period will begin.

Fill another sample cell (the blank) with 10 mL of sample.



10. When the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

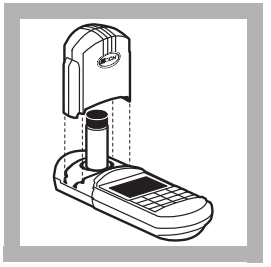


11. Press: **ZERO**

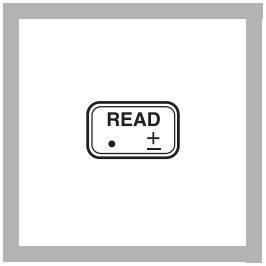
The cursor will move to the right, then the display will show:

0.00 mg/L NO3-N

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



12. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



13. Press: **READ**

The cursor will move to the right, then the result in mg/L NO_3^--N (or alternate form) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Note: *Rinse the sample cell and cylinder immediately after use to remove all cadmium particles.*

Note: *See Pollution Prevention and Waste Management for proper disposal of cadmium.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before running the test. For longer storage periods, adjust sample pH to 2 or less with sulfuric acid, ACS (about 2 mL per liter). Sample refrigeration is still required.

Before testing the stored sample, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution. Do not use mercury compounds as preservatives. Correct the test result for volume additions; see *Correction for Volume Additions* (*Section 1*) for more information.

Accuracy Check

Standard additions Method

a) Fill three 25-mL graduated mixing cylinders with 15 mL of sample.

b) Snap the neck off a Nitrate Nitrogen Ampule Standard Solution, 12.0 mg/L NO_3^--N.

c) Using the TenSette Pipet, add 0.1, 0.2, and 0.3 mL of the standard to the three samples. Stopper and mix well.

d) Analyze each sample as described above. The nitrate nitrogen concentration should increase 0.08 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* (Section 1) for more information.

Standard Solution Method

Prepare a 0.20 mg/L nitrate nitrogen standard by diluting 2.00 mL of a
10.0 mg/L Nitrate Nitrogen Standard Solution to 100.0 mL with deionized water. Use this standard in place of sample in Step 3.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 0.20-mg/L standard solution, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **0.20** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the curve adjustment. If you are using a reagent blank correction, the blank correction should be entered before the Standard Adjust feature is entered. See *Section 1*, *Standard Curve Adjustmen*t for more information.

Method Performance

Precision

In a single laboratory using a standard solution of 0.25 mg/L nitrate nitrogen (NO_3^--N) and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of $\pm$0.03 mg/L nitrate nitrogen.

Estimated Detection Limit

The estimated detection limit for program 55 is 0.01 mg/L NO_3^--N. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Calcium	100 mg/L
Chloride	Chloride concentrations above 100 mg/L will cause low results. The test may be used at high chloride concentrations (seawater) but a calibration must be done using standards spiked to the same chloride concentration.
Ferric iron	All levels
Nitrite	All levels: This method measures both the nitrate and nitrite in the sample. If nitrite is present, the nitrite nitrogen test Program 60 should be done on the sample. Pretreat the nitrate nitrogen sample with the following pretreatment. Then subtract the amount of nitrite found from the results of the LR nitrate nitrogen test using the pretreated sample. **1.** Add 30-g/L Bromine Water dropwise to the sample in Step 3 until a yellow color remains. Mix after each drop. **2.** Add one drop of 30-g/L Phenol Solution to destroy the yellow color. **3.** Proceed with the LR Nitrate procedure.
pH	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.
Strong oxidizing and reducing substances	Interfere at all levels

Summary of Method

Cadmium metal reduces nitrates present in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt which couples to chromotropic acid to form a pink-colored product.

Pollution Prevention and Waste Management

NitaVer 6 contains cadmium metal. Both samples and reagent blanks will contain cadmium (D006) at a concentration regulated as hazardous wastes by the Federal RCRA. Do not pour these solutions down the drain. See *Section 3* for more information on proper disposal of these materials.

REQUIRED REAGENTS

Low Range Nitrate Reagent Set (100 tests) 24298-00
Includes: (1) 21071-69, (1) 21072-49

Description	Quantity Required Per Test	Unit	Cat. No.
NitriVer 3 Nitrite Reagent Powder Pillows	1 pillow	100/pkg	21071-69
NitraVer 6 Nitrate Reagent Powder Pillows	1 pillow	100/pkg	21072-49

REQUIRED APPARATUS

Cylinder, graduated, mixing, 25 mL	1	each	1896-40
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Bromine Water, 30 g/L	29 mL*	2211-20
Nitrate Nitrogen Standard Solution, 10.0 mg/L as NO_3^--N	500 mL	307-49
Nitrate Nitrogen Standard Solution, Voluette ampule, 12 mg/L as NO_3^--N, 10 mL	16/pkg	14333-10
Phenol Solution, 30 g/L	29 mL	2112-20
Pretreatment Kit, contains: (1) 2112-20, (1) 2211-20	each	2268-00
Sodium Hydroxide Standard Solution, 5.0 N	50 mL* SCDB	2450-26
Sulfuric Acid, ACS	500 mL*	979-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker	each	21968-00
Dropper, for 29-mL bottle	each	2258-00
Flask, volumetric, Class A, 100 mL	each	14574-42
pH Indicator Paper, 1 to 11 pH	5-roll/pkg	391-33
pH Meter, *sens**ion***™*1*, portable, with electrode	each	51700-10
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 Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Pipet, volumetric, Class A, 2.00 mL	each	14515-36
Pipet Filler, safety bulb	each	14651-00
Thermometer, –20 to 110 °C	each	26357-02

Nitrate at these levels can also be determined directly using the Nitrate Ion Selective Electrode (Cat. No. 23488-00).

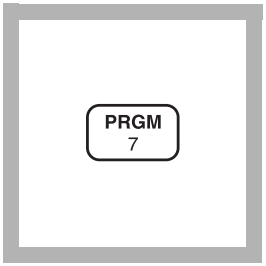
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Contact Hach for larger sizes

NITRITE, Low Range (0 to 0.350 mg/L NO_2^--N) For water, wastewater, seawater

Diazotization Method* (Powder Pillows or AccuVac Ampuls);
USEPA approved for reporting wastewater and drinking water analyses.



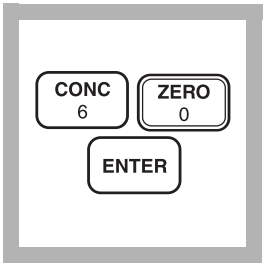
1. Enter the stored program number for nitrite nitrogen (NO_2^--N), powder pillows.

Press: **PRGM**

The display will show:

PRGM ?

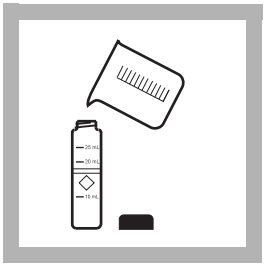
Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



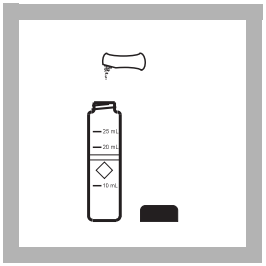
2. Press: **60 ENTER**

The display will show **mg/L, NO2-N** and the **ZERO** icon.

Note: *For alternate forms (NO_2^-, $NaNO_2$), press the* **CONC** *key.*



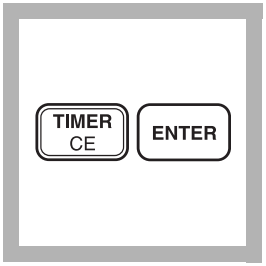
3. Fill a sample cell with 10 mL of sample.



4. Add the contents of one NitriVer 3 Nitrite Reagent Powder Pillow to the sample cell. Cap the cell and shake to dissolve.

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

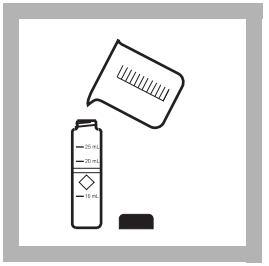
* *Federal Register*, 44(85) 25505 (May 1, 1979)



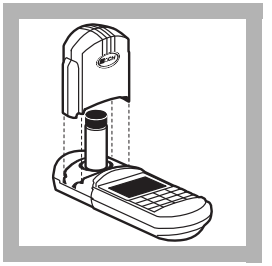
5. Press:
TIMER ENTER

A 15-minute reaction period will begin.

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

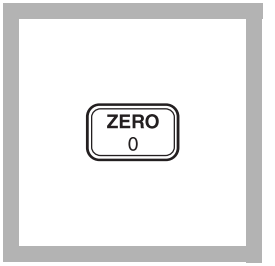


6. When the timer beeps, fill an empty sample cell with 10 mL of sample (the blank).



7. Wipe the outside of the sample cell with a towel. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *Wiping with a damp cloth, followed by a dry pne, removes fingerprints and other marks.*

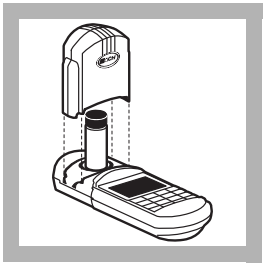


8. Press: **ZERO**

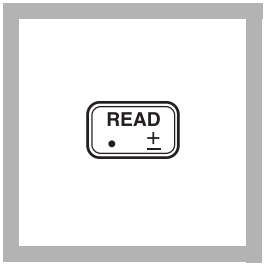
The cursor will move to the right, then the display will show:

0.000 mg/L NO2-N

Note: *If Reagent Blank Correction is on, the display may flash "limit." See Section 1.*



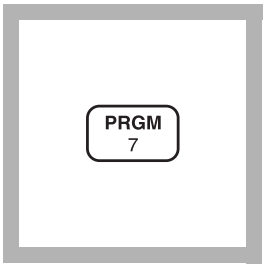
9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L nitrite nitrogen (or an alternate form) will be displayed.

Using AccuVac Ampuls



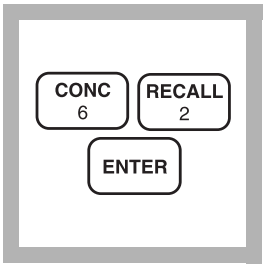
1. Enter the stored program number for nitrite nitrogen (NO_2^--N), AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

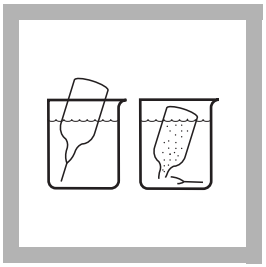
Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **62 ENTER**

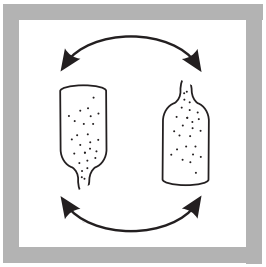
The display will show **mg/L, NO2-N** and the **ZERO** icon**.**

Note: *For alternate forms (NO_2^-, $NaNO_2$), press the* **CONC** *key.*



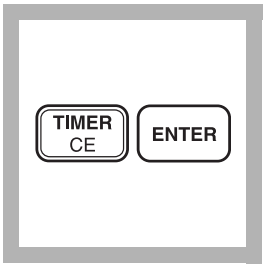
3. Collect at least 40 mL of sample in a 50-mL beaker. Fill a NitriVer 3 Nitrite AccuVac Ampul with the sample.

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



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

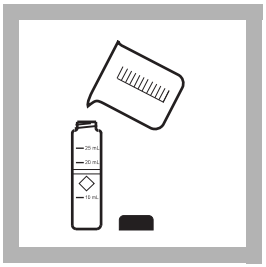
Note: *Accuracy is not affected by undissolved powder.*



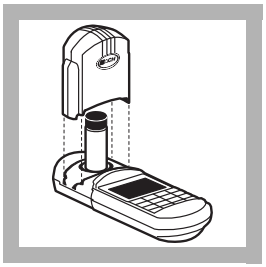
5. Press:
TIMER ENTER

A 15-minute reaction period will begin.

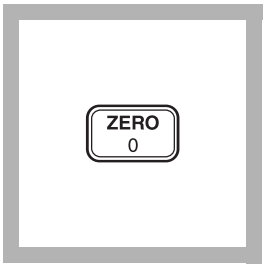
Note: *A pink color will develop if nitrite is present.*



6. When the timer beeps, fill a sample cell with at least 10 mL of sample (the blank).



7. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

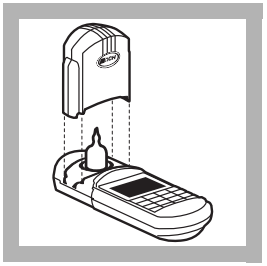


8. Press: **ZERO**

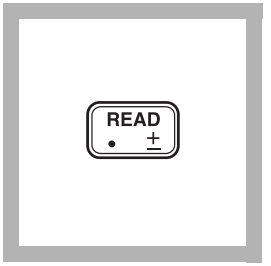
The cursor will move to the right, then the display will show:

0.000 mg/L NO2-N

Note: *If Reagent Blank Correction is on, the display may flash "limit." See Section 1.*



9. Place the AccuVac Ampul into the cell holder. Tightly cover the ampul with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L nitrite nitrogen will be displayed.

Sampling and Storage

Collect samples in clean plastic or glass bottles.

Store at 4 °C (39 °F) or lower and analyze within 48 hours. Warm to room temperature before running the test.

Do not use acid preservatives.

Remove the suspended solids by filtration.

Accuracy Check

Standard Solution Method

Pipet 5.00 mL of a fresh 250 mg/L NO_2^--N standard into a 250.0 mL volumetric flask. Dilute to the mark with deionized water. This makes a 5.00-mg/L intermediate standard. To prepare a 0.100-mg/L NO_2^--N standard solution, dilute 10.00 mL of the 5.00-mg/L intermediate standard to 500 mL in a volumetric flask. Prepare this solution immediately before use.

Run the test using the 0.100 mg/L NO_2^--N standard in place of the sample. Results should be between 0.090 and 0.110 mg/L NO_2^--N.

Method Performance

Precision

In a single laboratory, using a standard solution of 0.250 mg/L nitrite nitrogen and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.001 mg/L NO_2^--N for the powder pillow method and ±0.003 mg/L NO_2^--N for the
AccuVac method.

Estimated Detection Limit

The estimated detection limit for programs 60 and 62 is 0.005 mg/L NO_2^--N. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels
Antiminous ions	Interfere by causing precipitation
Auric ions	Interfere by causing precipitation
Bismuth ions	Interfere by causing precipitation
Chloroplatinate ions	Interfere by causing precipitation
Cupric ions	Cause low results
Ferric ions	Interfere by causing precipitation
Ferrous ions	Cause low results
Lead ions	Interfere by causing precipitation
Mercurous ions	Interfere by causing precipitation
Metavanadate ions	Interfere by causing precipitation
Nitrate	Very high levels of nitrate (>100 mg/L nitrate as N) appear to undergo a slight amount of reduction to nitrite, either spontaneously or during the course of the test. A small amount of nitrite will be found at these levels.
Silver ions	Interfere by causing precipitation
Strong oxidizing and reducing substances	Interfere at all levels

Summary of Method

Nitrite in the sample reacts with sulfanilic acid to form an intermediate diazonium salt. This couples with chromotropic acid to produce a pink colored complex directly proportional to the amount of nitrite present.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
NitriVer 3 Nitrite Reagent Powder Pillows	1 pillow	100/pkg	21071-69
or			
NitriVer 3 Nitrite Reagent AccuVac Ampuls	1 ampul	25/pkg	25120-25

REQUIRED APPARATUS

Beaker, 50 mL (for AccuVac procedure)	1	each	500-41H
or			
Sample Cells, 10-20-25 mL (powder pillow procedure)	2	6/pkg	24019-06

OPTIONAL REAGENTS

Nitrite Standard Solution, 250 mg/L as NO_2^--N		500 mL	23402-49
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
AccuVac Snapper Kit	each	24052-00
Flask, volumetric, 250 mL	each	14574-46
Flask, volumetric, 500 mL	each	14574-49
Pipet, serological, 10 mL	each	532-38
Pipet, TenSette, 1 to 10 mL	each	19700-01
Pipet Tips for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pipet Filler, safety bulb	each	14651-00
Thermometer, –20 to 110 °C	each	26357-02

For Technical Assistance, Price and Ordering

In the U.S.A. call 800-227-4224

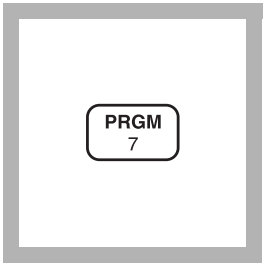
Outside the U.S.A.—Contact the Hach office or distributor serving you.

NITRITE, Low Range, Test 'N Tube (0–0.500 mg/L NO_2^--N)

Diazotization Method

For water, wastewater, and seawater

USEPA approved for wastewater analysis*



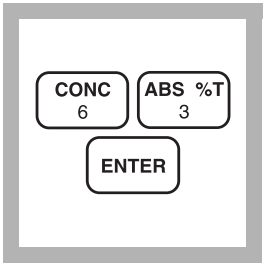
1. Enter the stored program number for nitrite nitrogen (NO_2^--N), Test 'N Tube.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



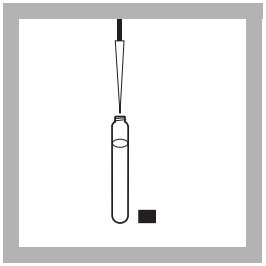
2. Press: **63 ENTER**

The display will show **mg/L, NO2-N** and the **ZERO** icon.

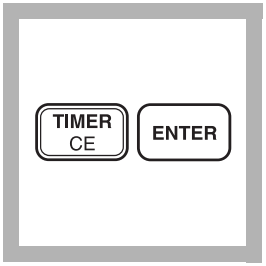
Note: *For alternate forms (NO_2^-, $NaNO_2$), press the* **CONC** *key.*

3. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert.

Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



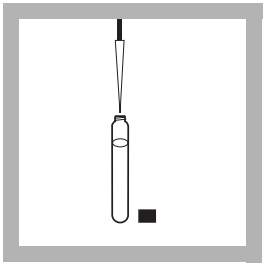
4. Fill a Test 'N Tube NitriVer® 3 Nitrite vial with 5 mL of sample. Cap and shake to dissolve powder. This is the prepared sample.



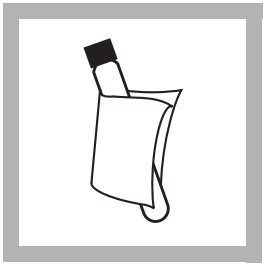
5. Press:
TIMER ENTER

A 20-minute reaction period will begin.

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

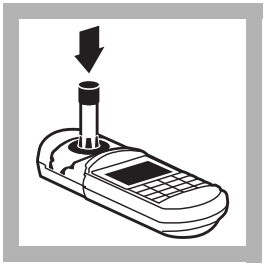


6. When the timer beeps, fill an empty Test 'N Tube vial with 5 mL of sample (the blank).



7. Clean the outside of the vials with a towel.

Note: *Wipe with a damp towel and follow with a dry one to remove fingerprints and other marks.*

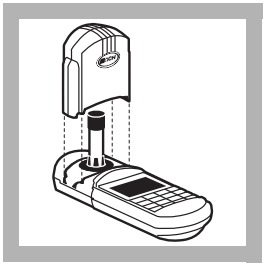


8. Place the blank in the vial adapter.

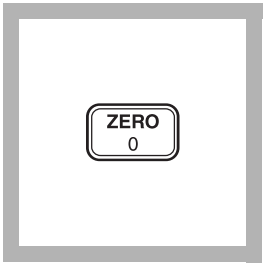
Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*

* *Federal Register,* 44(85) 25505 (May 1, 1979).



9. Cover the sample cell tightly with the instrument cap.

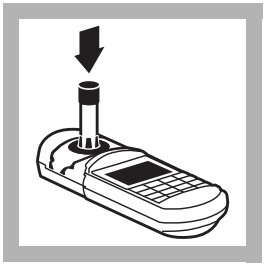


10. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.000 mg/L NO2-N

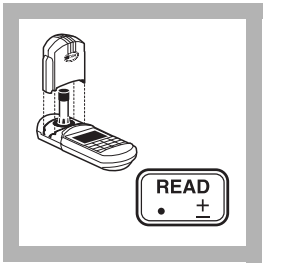
Note: *If the reagent blank correction is on, the display may flash "limit." See Section 1.*



11. Place the prepared sample in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



12. Tightly cover the sample cell with the instrument cap.

Press: **READ**

The cursor will move to the right, then the result in mg/L nitrite nitrogen (or an alternate form) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in clean plastic or glass bottles.

Store at 4 °C (39 °F) or lower and analyze within 48 hours. Warm to room temperature before running the test.

Do not use acid preservatives.

Remove suspended solids by filtration.

Accuracy Check

Standard Solution Method

Pipet 5.00 mL of a fresh Hach standard, 250 mg/L as NO_2^--N into a Class A 250-mL volumetric flask. Dilute to the line with deionized water to make a 5.00-mg/L intermediate standard. Pipet 10.00 mL of the 5.0-mg/L intermediate standard into a Class A 500-mL volumetric flask. Dilute to the line with deionized water to make a 0.100 mg/L NO_2^--N standard solution. Prepare immediately before use.

Run the test using the 0.100 mg/L NO_2^--N standard in place of the sample. Results should be between 0.090 and 0.110 mg/L NO_2^--N.

Method Performance

Precision

In a single laboratory, using a standard solution of 0.250 mg/L nitrite nitrogen and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.004 mg/L NO_2^--N.

Estimated Detection Limit

The estimated detection limit for program 63 is 0.006 mg/L NO_2^--N. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels
Antiminous ions	Interfere by causing precipitation
Auric ions	Interfere by causing precipitation
Bismuth ions	Interfere by causing precipitation
Chloroplatinate ions	Interfere by causing precipitation
Cupric ions	Cause low results
Ferric ions	Interfere by causing precipitation
Ferrous ions	Cause low results
Lead ions	Interfere by causing precipitation
Mercurous ions	Interfere by causing precipitation
Metavanadate ions	Interfere by causing precipitation
Nitrate	Very high levels of nitrate (>100 mg/L nitrate as N) appear to undergo a slight amount of reduction to nitrite, either spontaneously or during the course of the test. A small amount of nitrite will be found at these levels.
Silver ions	Interfere by causing precipitation
Strong oxidizing and reducing substances	Interfere at all levels

Summary of Method

Nitrite in the sample reacts with sulfanilic acid to form an intermediate diazonium salt. This couples with chromotropic acid to produce a pink-colored complex directly proportional to the amount of nitrite present.

REQUIRED REAGENTS

Description	Cat. No.
NitriVer® 3 Nitrite, Low Range Test 'N Tube Reagent Set (50 tests)	26083-45
Includes:	
(50) NitriVer® 3 Nitrite Test 'N Tube Vials	*
Vials, 6 x 100 mm, 6/pkg	22758-06
Caps, for 22758-06 vials, 6/pkg	22411-06
Deionized water, 100-mL	272-42

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
COD/TNT Adapter	1	each	48464-00
Test Tube Rack	1-3	each	18641-00
Pipet, TenSette, 1 to 10 mL	1	each	19700-10
Pipet Tips for 19700-10 TenSette Pipet	1	50/pkg	21997-96

OPTIONAL REAGENTS

Nitrite Standard Solution, 250 mg/L as NO_2^--N	500	mL	23402-49
Water, deionized	4	L	272-56

OPTIONAL APPARATUS

Flask, volumetric, 250 mL		each	14574-46
Flask, volumetric, 500 mL		each	14574-49
Pipet, volumetric, Class A, 10.00 mL		each	14515-38

For Technical Assistance, Price and Ordering

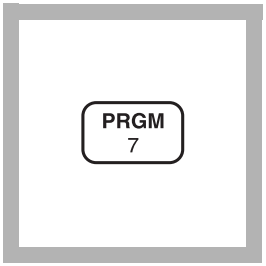
In the U.S.A. call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Not available separately.

OXYGEN DEMAND, CHEMICAL (20 to 1,000 mg/L) For water and wastewater

Manganese III Digestion Method* (without chloride removal)



1. Enter the stored program number for Manganese III COD.

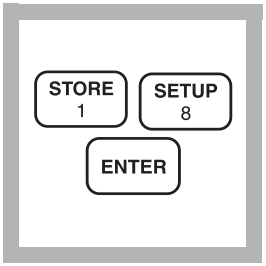
Press: **PRGM**

The display will show:

PRGM ?

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

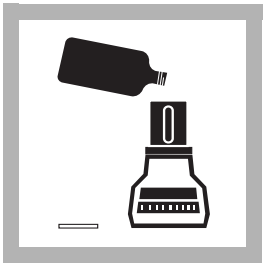
Note: *Preheat the COD Reactor to 150 °C for use later in the procedure.*



2. Press: **18 ENTER**

The display will show **mg/L, COD** and the **ZERO** icon**.**

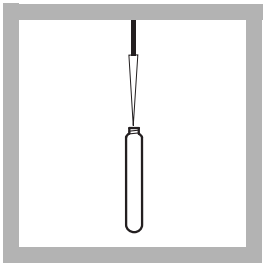
Note: *For alternate forms (O_2), press the* **CONC** *key.*



3. Homogenize 100 mL of sample for 30 seconds in a blender.

Note: *Blending promotes even distribution of solids and improves accuracy and reproducibility.*

Note: *Continue mixing the sample while pipetting if suspended solids are present.*



4. If chloride is not present in significant amounts†, pipet 0.50 mL of homogenized sample into a Mn III COD vial. Cap and invert several times to mix.

Note: *If the sample COD value is not between 20-1000 mg/L dilute the sample with deionized water to obtain a range of 20-1000 mg/L COD. Multiply the final result by the dilution factor.*

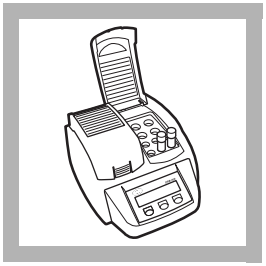
† To determine if chloride will interfere, run the sample with and without the chloride removal procedure and compare the results.

Caution: Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings and the safety section of this manual. Wear appropriate eye protection and appropriate clothing. If contact occurs, flush the affected area with running water. Follow all instructions carefully.

* U.S. Patent 5,556,787

5. Prepare a blank (see note) by substituting 0.50 mL of deionized water for the sample. Continue with step 9 of this procedure.

Note: *The reagent blank is stable and can be reused. Verify reagent blank quality by measuring the absorbance of the blank vs. a clean COD vial filled with deionized water. The absorbance range should be about 1.36-1.43.*

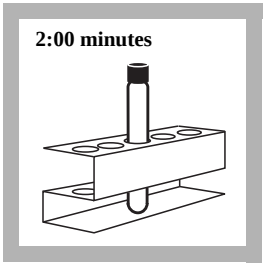


6. Place the vials in the DRB 200 Reactor that is preheated to 150 °C. Digest for 1 hour.

Note: *Boiling sample in the vials during digestion indicates the vial is not properly sealed; test results will be invalid.*

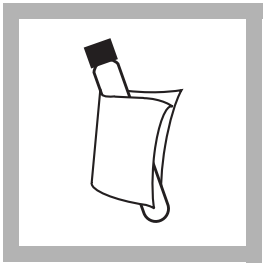
Note: *Samples can be digested up to 4 hours to oxidize more resistant organics. The prepared blank must be treated in the same manner.*

Note: *See DRB 200 user manual for selecting pre-programmed temperature applications.*



7. Remove the vials and place them in a cooling rack for two minutes to air cool. Then cool the vials to room temperature in a cool water bath or running tap water. This usually takes about three minutes.

Note: *Occasionally a vial will develop a colorless upper layer and a purple lower layer. Invert the vial several times to mix and proceed. This will not affect test results.*

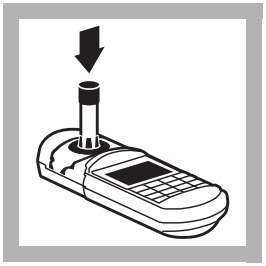


8. Remove the vials from the water and wipe with a clean, dry paper towel.

Invert the vials several times to mix.

9. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

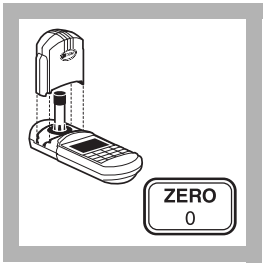
Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



10. Place the blank in the sample cell adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



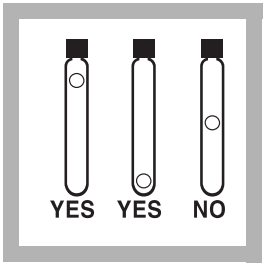
11. Tightly cover the sample cell with the instrument cap.

Note: *Clean the COD vial with a towel to remove fingerprints or other marks.*

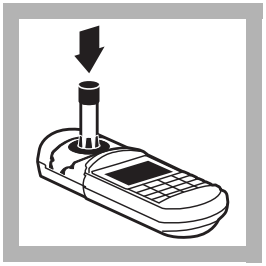
Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L COD



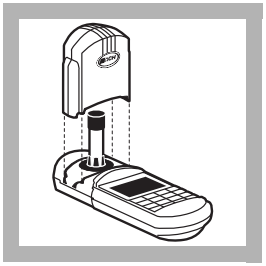
12. If the chloride removal was done, make sure the filter disc is not suspended in the middle of the vial; it can interfere with the instrument reading. Move it with gentle swirling or by lightly tapping the vial on the table top.



13. Place the sample in the adapter.

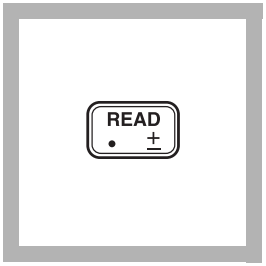
Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



14. Tightly cover the sample cell with the instrument cap.

Note: *Clean the COD vial with a towel to remove fingerprints or other marks.*



15. Press: **READ**

The cursor will move to the right, then the result in mg/L COD will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Note: *Adjust the result for any sample dilution in Steps 4 or 6.*

Sampling and Storage

Collect samples in clean glass bottles. Use plastic bottles only if they are known to be free of organic contamination. Test biologically active samples as soon as possible. Homogenize samples containing solids to assure representative samples. Samples treated with concentrated sulfuric acid to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C may be stored up to 28 days. Correct results for volume additions; see *Correcting for Volume Additions* (*Section 1*) for more information.

Accuracy Check

Standard Solution Method

Prepare an 800 mg/L COD standard solution by adding 0.6808 g of
dried (103 °C, overnight) potassium acid phthalate (KHP) to 1 liter of deionized water. Use 0.50 mL of this solution (0.60 mL for the chloride removal procedure) as the sample volume. The result should be
800 ±26 mg/L COD.

An 800 mg/L COD solution can also be purchased directly from Hach (see *Optional Reagents*).

Method Performance (for Manganic III COD without the chloride removal procedure)

Precision

In a single laboratory, using a standard solution of 800 mg/L COD and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±23 mg/L COD.

Estimated Detection Limit (EDL)

The EDL for program 18 is 14 mg/L COD. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Inorganic materials may also be oxidized by trivalent manganese and constitute a positive interference when present in significant amounts. Chloride is the most common interference and is removed by sample pretreatment with the Chloride Removal Cartridge. If chloride is known to be absent or present in insignificant levels, the pretreatment can be omitted. A simple way to determine if chloride will affect test results is to run

routine samples with and without the chloride removal, then compare results. Other inorganic interferences (i.e., nitrite, ferrous iron, sulfide) are not usually present in significant amounts. If necessary, these interferences can be corrected for after determining their concentrations with separate methods and adjusting the final COD test
results accordingly.

Ammonia nitrogen is known to interfere in the presence of chloride; it does not interfere if chloride is absent.

Summary of Method

Chemical oxygen demand (COD) is defined as "... a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant" (APHA Standard Methods, 19th ed., 1995). Trivalent manganese is a strong, non-carcinogenic chemical oxidant that changes quantitatively from purple to colorless when it reacts with organic matter. It typically oxidizes about 80% of the organic compounds. Studies have shown that the reactions are highly reproducible and test results correlate closely to Biochemical Oxygen Demand (BOD) values and hexavalent chromium COD tests. None of the oxygen demand tests provide 100% oxidation of all
organic compounds.

A calibration is provided which is based on the oxidation of Potassium Acid Phthalate (KHP). A different response may be seen in analyzing various wastewaters. The KHP calibration is adequate for most applications. The highest degree of accuracy is obtained when test results are correlated to a standard reference method such as BOD or one of the chromium COD methods. Special waste streams or classes will require a separate calibration to obtain a direct mg/L COD reading or to generate a correction factor for the precalibrated KHP response. The sample digestion time can be extended up to 4 hours for samples which are difficult to oxidize.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Manganese III COD Reagent Vials, 20-1000 mg/L	1	25/pkg	26234-25
Sulfuric Acid, concentrated	1 mL	4 Kg	979-09
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Adapter, COD/TNT	1	each	48464-00
Blender, Osterizer, 120 Vac, 14-speed	1	each	26747-00
Blender Container, 118 mL	1	2/pkg	26748-00
Cap, with inert Teflon liner, for mixing bottle	varies	12/pkg	24018-12
DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes			LTV082.52.40001
Forceps, extra fine point	1	each	26696-00
Mixing Bottle, glass, for sample + acid	1	each	24276-06
Pipet, TenSette, 1.0 to 10.0 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette	2	250/pkg	21997-25
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette	2	1000/pkg	21856-28
Test Tube Rack, stainless steel	1	each	18641-00

OPTIONAL REAGENTS

COD Standard Solution, 800 mg/L COD		200 mL	26726-29
Oxygen Demand Standard (BOD, COD, TOC), 10-mL Ampules		16/pkg	28335-10
Potassium Acid Phthalate		500 g	315-34
Wastewater Effluent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)		500 mL	28332-49
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)		500 mL	28331-49

OPTIONAL APPARATUS

Dispenser for sulfuric acid		each	25631-37
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm			LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm			LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm			LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm			LTV082.52.30001

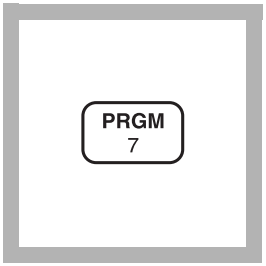
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

OXYGEN DEMAND, CHEMICAL (20 to 1,000 mg/L) For water and wastewater

Manganese III Digestion Method* (with chloride removal)



1. Enter the stored program number for Manganese III COD.

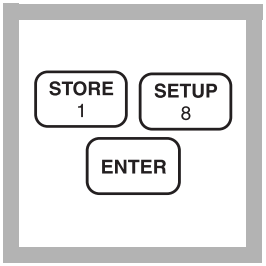
Press: **PRGM**

The display will show:

PRGM ?

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

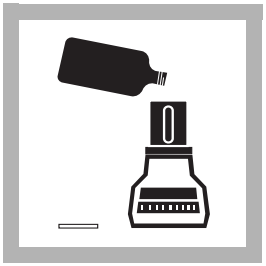
Note: *Preheat the COD Reactor to 150 °C for use later in the procedure.*



2. Press: **18 ENTER**

The display will show **mg/L, COD** and the **ZERO** icon**.**

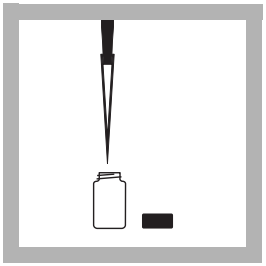
Note: *For alternate forms (O_2), press the* **CONC** *key.*



3. Homogenize 100 mL of sample for 30 seconds in a blender.

Note: *Blending promotes even distribution of solids and improves accuracy and reproducibility.*

Note: *Continue mixing the sample while pipetting if suspended solids are present.*



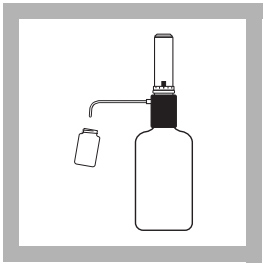
Chloride Removal Procedure

4. Using a TenSette Pipet or a pipet and safety bulb, pipet 9.0 mL of homogenized sample into an empty glass mixing cell. If the sample COD exceeds 1000 mg/L, dilute the sample as described in *Table 1*.

Note: *If suspended solids are present, continue mixing the sample while pipetting.*

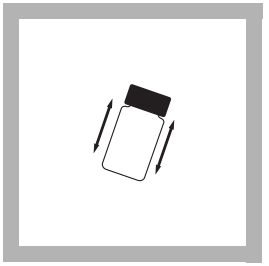
Caution: Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings and the safety section of this manual. Wear appropriate eye protection and appropriate clothing. If contact occurs, flush the affected area with running water. Follow all instructions carefully.

* U.S. Patent 5,556,787



5. Using an automatic dispenser or TenSette Pipet, add 1.0 mL of concentrated sulfuric acid to the mixing cell.

Note: *Mixing concentrated sulfuric acid and water is not additive. Adding 1.0 mL of concentrated sulfuric acid to 9.0 mL of sample does not result in a final volume of 10.0 mL. This factor is built into the calibration curve.*



6. Cap the cell tightly and invert it several times. The solution will become hot. Cool to room temperature before proceeding.

Note: *Acidified samples are stable for several months when refrigerated at 4 °C.*

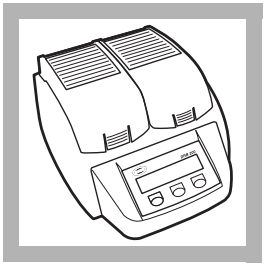
PREPARE BLANK

7. Prepare a blank (see note) by repeating Steps 4-6, substituting 9.0 mL of deionized water for the sample.

Note: *The reagent blank is stable and can be reused. Verify reagent blank quality by measuring the absorbance of the blank vs. a clean COD vial filled with deionized water. The absorbance range, when using chloride removal, should be about 1.31-1.36.*

Note: *Use a clean pipet or rinse it thoroughly.*

Note: *One blank must be run with each lot of reagents. Run all samples and blanks with the same lot of vials (lot number is on the container label).*



8. If not already on, turn on the DRB 200 Reactor and heat to 150 °C.

Note: *See DRB 200 user manual for selecting pre-programmed temperature applications.*

Table 1 Dilution Table (for use with Chloride Removal Procedure Only)

Sample (mL)	Deionized Water (mL)	Range (mg/L COD)	Multiplication Factor
6.0	3.0	30-1500	1.5
3.0	6.0	60-3000	3
1.0	8.0	180-9000	9
0.5	8.5	360-18000	18

All dilutions require that the ratio of sample to sulfuric acid remain at 9:1. For other dilutions that are not listed in Table 1, simply add the sample volume + deionized water and divide by the sample volume to obtain the multiplication factor.

Example:

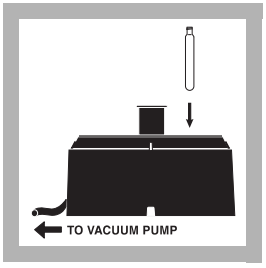
Dilute the sample to a range of 90-4500 mg/L COD

Sample Volume (2.0 mL) + Deionized water (7.0 mL) = Total Volume (9.0 mL)

$$\text{Multiplication Factor} = \frac{\text{Total Volume}}{\text{Sample Volume}} = \frac{9.0\ \text{mL}}{2.0\ \text{mL}} = 4.5$$

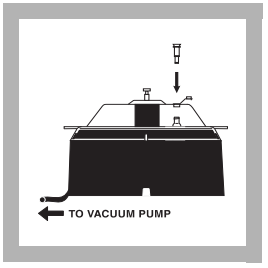
Standard test range is 20-1000 mg/L COD. Example Test Range = 4.5 (20) to 4.5 (1000) = 90-4500 mg/L COD

It is best to use 0.5 mL or more of sample for diluting. If sample values exceed 18,000 mg/L COD, use a separate sample dilution before the sample chloride removal procedure.

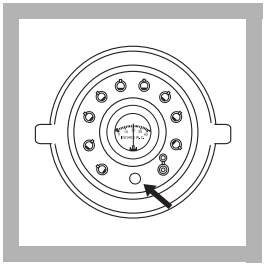


9. Label each Mn III COD vial and remove the cap. Place the vial in one of the numbered holes in the Vacuum Pretreatment Device (VPD)* base.

Note: *The VPD must be attached to a vacuum pump (not an aspirator-type vacuum) that can create a vacuum of 20 to 25 inches of mercury.*

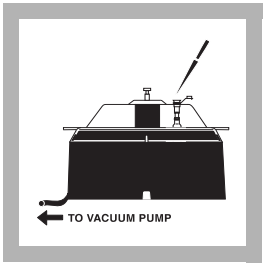


10. Place the VPD top on the base. Insert a fresh Chloride Removal Cartridge (CRC)** directly above each Mn III COD Reagent Vial. Plug any open holes in the VPD top using the stoppers provided.



11. Turn the vacuum pump on and adjust the vacuum regulator valve on top of the VPD until the internal gauge reads 20 inches of water.

Note: *The optimum setting allows the sample to flow through the CRC in about 30 to 45 seconds.*

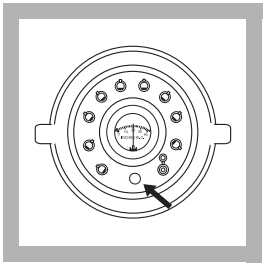


12. Pipet 0.60 mL of acidified sample (made in Steps 4-6) into the CRC. Pipet 0.60 mL of acidified blank into another CRC.

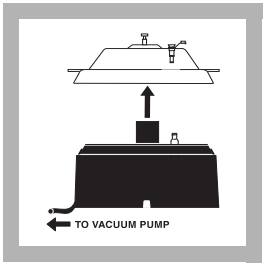
Note: *If the sample does not flow through the CRC, increase the vacuum until flow starts, then reduce the vacuum to 20 inches of water. Proceed as usual.*

* Patent Pending.

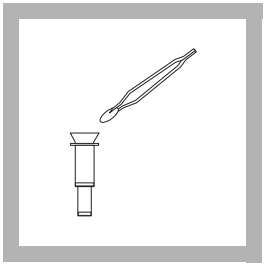
** U.S. patents 5,667,754 and 5,683,914.



13. Close the vacuum regulator valve completely to achieve full vacuum. After one minute under full vacuum, slide the VPD back and forth several times to dislodge any drops clinging to the cartridge.



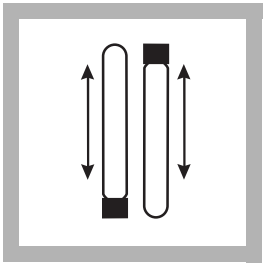
14. Open the VPD regulator valve to release the vacuum. Turn the pump off. Remove the VPD top and set it beside the base.



15. Use forceps to remove the filter from the top of each CRC. Place each filter in the corresponding Mn III COD Vial (use the numbers on the VPD as a guide).

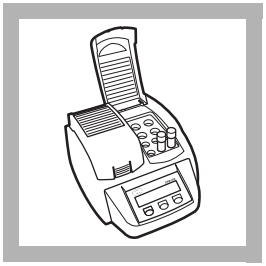
Note: *If the sample does not contain suspended solids, it is not necessary to transfer the filter to the digestion vial.*

Note: *To avoid cross contamination, clean forceps tips between samples by wiping with a clean towel or rinsing with deionized water.*



16. Remove the Mn III COD vial from the vacuum chamber and replace the original cap. Screw the cap on tightly. Invert several times to mix.

Note: *Dispose of the used Chloride Removal Cartridge. Do not reuse it.*

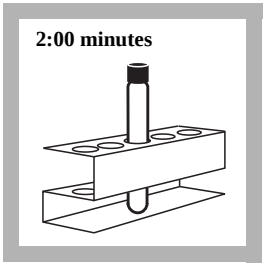


17. Place the vials in the DRB 200 Reactor that is preheated to 150 °C. Digest for 1 hour.

Note: *Boiling sample in the vials during digestion indicates the vial is not properly sealed; test results will be invalid.*

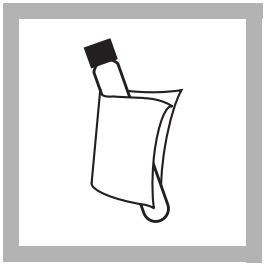
Note: *Samples can be digested up to 4 hours to oxidize more resistant organics. The prepared blank must be treated in the same manner.*

Note: *See DRB 200 user manual for selecting pre-programmed temperature applications.*



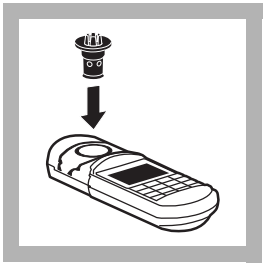
18. Remove the vials and place them in a cooling rack for two minutes to air cool. Then cool the vials to room temperature in a cool water bath or running tap water. This usually takes about three minutes.

Note: *Occasionally a vial will develop a colorless upper layer and a purple lower layer. Invert the vial several times to mix and proceed. This will not affect test results.*



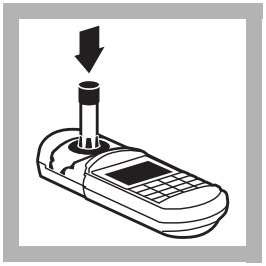
19. Remove the vials from the water and wipe with a clean, dry paper towel.

Invert the vials several times to mix.



20. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

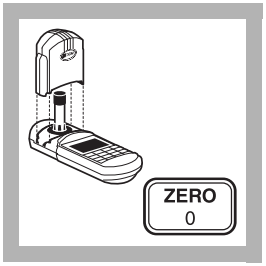
Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



21. Place the blank in the sample cell adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



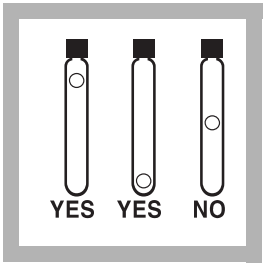
22. Tightly cover the sample cell with the instrument cap.

Note: *Clean the COD vial with a towel to remove fingerprints or other marks.*

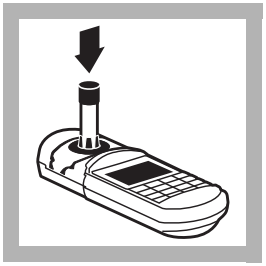
Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L COD



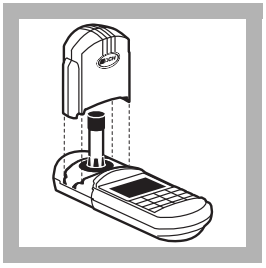
23. If the chloride removal was done, make sure the filter disc is not suspended in the middle of the vial; it can interfere with the instrument reading. Move it with gentle swirling or by lightly tapping the vial on the table top.



24. Place the sample in the adapter.

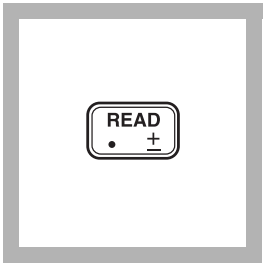
Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



25. Tightly cover the sample cell with the instrument cap.

Note: *Clean the COD vial with a towel to remove fingerprints or other marks.*



26. Press: **READ**

The cursor will move to the right, then the result in mg/L COD will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Note: *Adjust the result for any sample dilution.*

Sampling and Storage

Collect samples in clean glass bottles. Use plastic bottles only if they are known to be free of organic contamination. Test biologically active samples as soon as possible. Homogenize samples containing solids to assure representative samples. Samples treated with concentrated sulfuric acid to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C may be stored up to 28 days. Correct results for volume additions; see *Correcting for Volume Additions* (*Section 1*) for more information.

Accuracy Check

Standard Solution Method

Prepare an 800 mg/L COD standard solution by adding 0.6808 g of
dried (103 °C, overnight) potassium acid phthalate (KHP) to 1 liter of deionized water. Use 0.50 mL of this solution (0.60 mL for the chloride removal procedure) as the sample volume. The result should be
800 ±26 mg/L COD.

An 800 mg/L COD solution can also be purchased directly from Hach (see *Optional Reagents*).

Method Performance (for Manganic III COD without the chloride removal procedure)

Precision

In a single laboratory, using a standard solution of 800 mg/L COD and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±23 mg/L COD.

Estimated Detection Limit (EDL)

The EDL for program 18 is 14 mg/L COD. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Inorganic materials may also be oxidized by trivalent manganese and constitute a positive interference when present in significant amounts. Chloride is the most common interference and is removed by sample pretreatment with the Chloride Removal Cartridge. If chloride is known to be absent or present in insignificant levels, the pretreatment can be omitted. A simple way to determine if chloride will affect test results is to run

routine samples with and without the chloride removal, then compare results. Other inorganic interferences (i.e., nitrite, ferrous iron, sulfide) are not usually present in significant amounts. If necessary, these interferences can be corrected for after determining their concentrations with separate methods and adjusting the final COD test results accordingly.

Ammonia nitrogen is known to interfere in the presence of chloride; it does not interfere if chloride is absent.

Summary of Method

Chemical oxygen demand (COD) is defined as "... a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant" (APHA Standard Methods, 19th ed., 1995). Trivalent manganese is a strong, non-carcinogenic chemical oxidant that changes quantitatively from purple to colorless when it reacts with organic matter. It typically oxidizes about 80% of the organic compounds. Studies have shown that the reactions are highly reproducible and test results correlate closely to Biochemical Oxygen Demand (BOD) values and hexavalent chromium COD tests. None of the oxygen demand tests provide 100% oxidation of all organic compounds.

A calibration is provided which is based on the oxidation of Potassium Acid Phthalate (KHP). A different response may be seen in analyzing various wastewaters. The KHP calibration is adequate for most applications. The highest degree of accuracy is obtained when test results are correlated to a standard reference method such as BOD or one of the chromium COD methods. Special waste streams or classes will require a separate calibration to obtain a direct mg/L COD reading or to generate a correction factor for the precalibrated KHP response. The sample digestion time can be extended up to 4 hours for samples which are difficult to oxidize.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Chloride Removal Cartridges (CRC)	1	25/pkg	26618-25
Manganese III COD Reagent Vials, 20-1000 mg/L	1	25/pkg	26234-25
Sulfuric Acid, concentrated	1 mL	4 Kg	979-09
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Adapter, COD/TNT	1	each	48464-00
Blender, Osterizer, 120 Vac, 14-speed	1	each	26747-00
Blender Container, 118 mL	1	2/pkg	26748-00
Cap, with inert Teflon liner, for mixing bottle	varies	12/pkg	24018-12
DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes			LTV082.52.40001
Forceps, extra fine point	1	each	26696-00
Mixing Bottle, glass, for sample + acid	1	each	24276-06
Pipet, TenSette, 1.0 to 10.0 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette	2	250/pkg	21997-25
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette	2	1000/pkg	21856-28
Test Tube Rack, stainless steel	1	each	18641-00
Vacuum Pretreatment Device (VPD)	1	each	49000-00
Vacuum Pump, 115 V	1	each	14697-00
Vacuum Pump, 230V	1	each	14697-02

OPTIONAL REAGENTS

COD Standard Solution, 800 mg/L COD	200 mL	26726-29
Oxygen Demand Standard (BOD, COD, TOC), 10-mL Ampules	16/pkg	28335-10
Potassium Acid Phthalate	500 g	315-34
Wastewater Effluent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28332-49
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28331-49

OPTIONAL APPARATUS

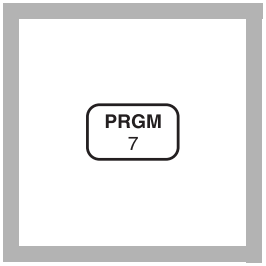
Dispenser for sulfuric acid	each	25631-37
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm		LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm		LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm		LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm		LTV082.52.30001

For Technical Assistance, Price and Ordering
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

OXYGEN, DISSOLVED, High Range (0 to 15.0 mg/L O_2)

HRDO Method

For water and wastewater

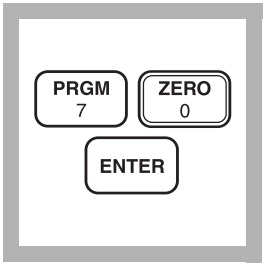


1. Enter the stored program number for dissolved oxygen, high range.

Press: **PRGM**

The display will show:

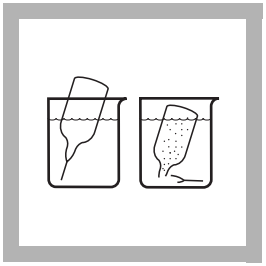
PRGM ?



2. Press: **70 ENTER**

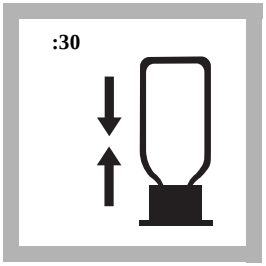
The display will show **mg/L, O2** and the **ZERO** icon.

3. Fill a sample cell (the blank) with at least 10 mL of sample. Fill a blue ampul cap with sample. Collect at least 40 mL of sample in a 50-mL beaker.



4. Fill a High Range Dissolved Oxygen AccuVac Ampul with sample.

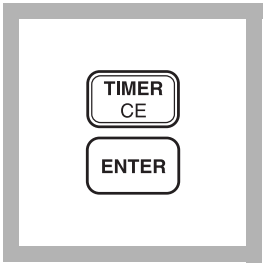
Note: *Keep the tip immersed while the ampul fills completely.*



5. Without inverting the ampul, immediately place the ampul cap that has been filled with sample securely over the tip of the ampul. Shake for about 30 seconds.

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

Note: *The cap prevents contamination with atmospheric oxygen.*

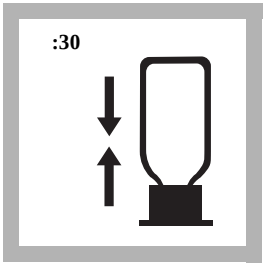


6. Press:

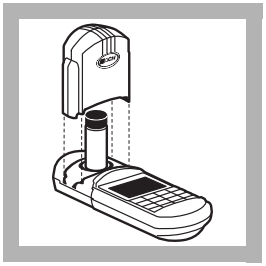
TIMER ENTER

A 2-minute reaction period will begin.

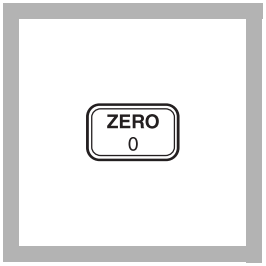
Note: *The two-minute period allows oxygen which was degassed during aspiration to redissolve in the sample and react.*



7. When the timer beeps, shake the ampul for 30 seconds.



8. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

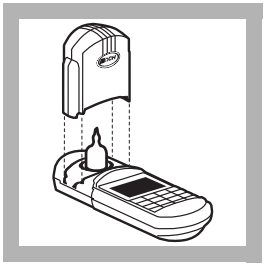


9. Press: **ZERO**

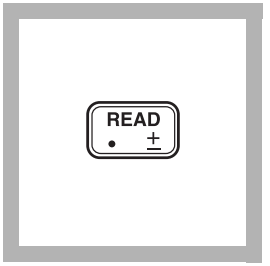
The cursor will move to the right, then the display will show:

0.0 mg/L O2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



10. Place the AccuVac ampul into the cell holder. Tightly cover the ampul with the instrument cap. Wait approximately 30 seconds for the air bubbles to disperse from the light path.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L O_2 will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

The main consideration in sampling with the High Range Dissolved Oxygen AccuVac Ampul is to prevent the sample from becoming contaminated with atmospheric oxygen. This is accomplished by capping the ampul with an ampul cap in the interval between breaking open the ampul and reading the absorbance. If the ampul is securely capped, it should be safe from contamination for several hours. The absorbance will decrease by approximately 3% during the first hour and will not change significantly afterwards.

Sampling and sample handling are important considerations in obtaining meaningful results. The dissolved oxygen content of the water being tested can be expected to change with depth, turbulence, temperature, sludge deposits, light, microbial action, mixing, travel time and other factors. A single dissolved oxygen test rarely reflects the accurate over-all condition of a body of water. Several samples taken at different times, locations and depths are recommended for most reliable results. Samples must be tested immediately upon collection although only a small error results if the absorbance reading is taken several hours later.

Accuracy Check

The results of this procedure may be compared with the results of a dissolved oxygen meter (Cat. No. 51815-01).

Method Performance

Precision

In a single laboratory, using a standard solution of 8.0 mg/L O_2 determined by the Winkler method and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of
±0.41 mg/L O_2.

Estimated Detection Limit

The estimated detection limit for program 70 is 0.10 mg/L O_2. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Cr^{3+}	Greater than 10 mg/L
Cu^{2+}	Greater than 10 mg/L
Fe^{2+}	Greater than 10 mg/L
Mg^{2+}	Magnesium is commonly present in seawater and causes a negative interference. If the sample contains more than 50% seawater, the oxygen concentration obtained by this method will be 25% less than the true oxygen concentration. If the sample contains less than 50% seawater, the interference will be less than 5%.
Mn^{2+}	Greater than 10 mg/L
Ni^{2+}	Greater than 10 mg/L
NO_2^-	Greater than 10 mg/L

Summary of Method

The High Range Dissolved Oxygen AccuVac Ampul contains reagent vacuum sealed in a 12-mL ampul. When the AccuVac ampul is broken open in a sample containing dissolved oxygen, a yellow color forms, which turns purple as the oxygen reacts with the reagent. The color developed is proportional to the concentration of dissolved oxygen.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
High Range Dissolved Oxygen AccuVac Ampuls, with 2 reusable ampul caps	1 ampul	25/pkg	25150-25

REQUIRED APPARATUS

Beaker, 50 mL	1	each	500-41H
Caps, ampul, blue	varies	25/pkg	1731-25
Sample Cell, 10-20-25 mL, w/ cap	1	6/pkg	24019-06

OPTIONAL REAGENTS AND APPARATUS

AccuVac Dissolved Oxygen Sampler	each	24051-00
AccuVac Snapper Kit	each	24052-00
AccuVac Drainer	each	41036-00
BOD bottle and stopper, 300 mL	each	621-00
Dissolved Oxygen Meter, Portable HQ 10	each	51815-01
Dissolved Oxygen Reagent Set (Buret Method)	100 tests	23514-00
Dissolved Oxygen Reagent Set (Digital Titrator Method)	50 tests	22722-00

Dissolved oxygen may also be determined by titrimetric methods. Request Publication 8042 for additional information.

For Technical Assistance, Price and Ordering

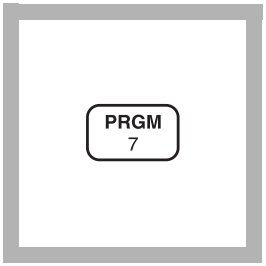
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

pH (6.5 to 8.5 pH units)

Colorimetric pH Determination Using Phenol Red

For water and wastewater

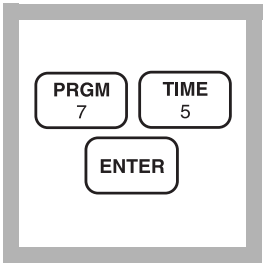


1. Enter the stored program number for the pH method.

Press: **PRGM**

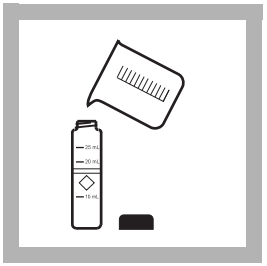
The display will show:

PRGM ?

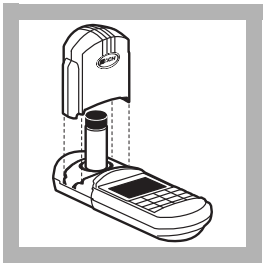


2. Press: **75 ENTER**

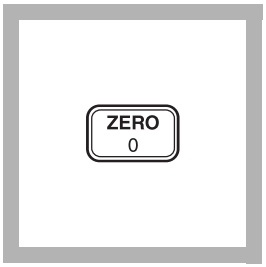
The display will show **PH** and the **ZERO** icon.



3. Fill a sample cell with 10 mL of sample (the blank).



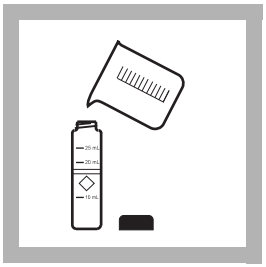
4. Place the blank in the cell holder. Tightly cover the sample cell with the instrument cap.



5. Press: **ZERO**

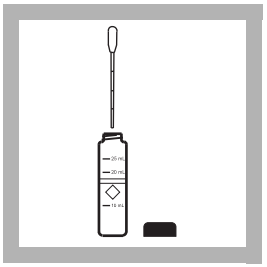
The cursor will move to the right, then the display will show:

6.0 PH

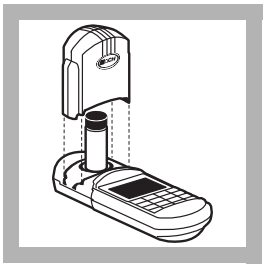


6. Fill another cell with 10 mL of sample.

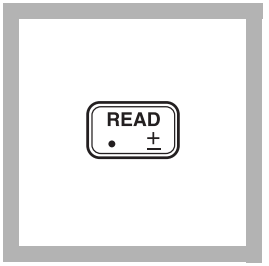
Note: *Sample temperature must be 21-29 °C.*



7. Using a disposable dropper, add 1 mL of Phenol Red Indicator Solution to the cell (the prepared sample). Cap the sample cell and invert twice to mix.



8. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



9. Press: **READ**

The cursor will move to the right, then the result in pH units will be displayed.

Note: *Use of the Standard Adjust feature is highly recommended. See* Accuracy Check.

Note: *Any reading below 6.5 pH units will be erroneous.*

Sampling and Storage

Analyze samples immediately for best results.

Accuracy Check

Standard Solution Method
Using a clear pH 7.0 buffer solution as the sample, perform the pH procedure as described above.

Method Performance

Precision
In a single laboratory using a standard solution of pH 7.0 and two lots of reagent with the instrument, a single operator obtained a standard deviation of less than 0.1 pH units.

Estimated Detection Limit
The estimated detection limit for program 75 is a pH of 6.5.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 7.0 buffer solution, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **7.0** to edit the standard concentration to match that of the standard used. See *Section 1, Standard Curve Adjustmen*t for more information. Press **ENTER** to complete the curve adjustment.

Interferences

Chlorine does not interfere at levels of 6 mg/L or lower.

Salt water (sea water) will interfere and cannot be analyzed using this method.

Summary of Method

This method uses a sulfonphthalein indicator (Phenol Red) to determine pH colorimetrically. Phenol Red has a working range of pH 6.8 (yellow) to 8.2 (red).

REQUIRED REAGENTS & APPARATUS

Description	Quantity Required Per Test	Units	Cat. No.
Dropper, 0.5 & 1.0 mL marks	1	20/pkg	21247-20
Phenol Red Indicator Solution, spec grade	1.0 mL	50 mL	26575-12
Sample Cells, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

pH 7.0 Buffer Solution		500 mL	12222-49

OPTIONAL APPARATUS

Description	Units	Cat. No.
Thermometer, -20 to 110 °C, Non-Mercury	each	26357-02

For Technical Assistance, Price and Ordering

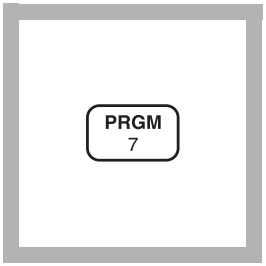
In the U.S.A. call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

PHOSPHORUS, REACTIVE (0 to 30.0 mg/L PO_4^{3-})

Amino Acid Method*

For water, wastewater, seawater



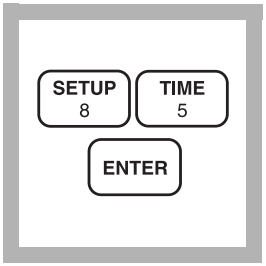
1. Enter the stored program number for reactive phosphate (PO_4^{3-}), amino acid method.

Press: **PRGM**

The display will show:

PRGM ?

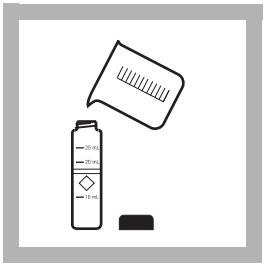
Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



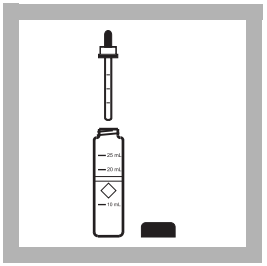
2. Press: **85 ENTER**

The display will show **mg/L, PO4** and the **ZERO** icon.

Note: *For alternate forms (P, P_2O_5), press* **CONC**.

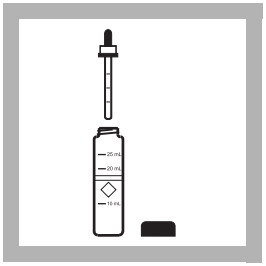


3. Fill a 25-mL sample cell with 25 mL of sample.



4. Add 1 mL of Molybdate Reagent using a 1-mL calibrated dropper.

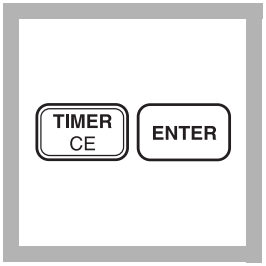
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



5. Add 1 mL of Amino Acid Reagent Solution. Cap and invert several times to mix (the prepared sample).

Note: *A blue color will form if phosphate is present.*

Note: *You may substitute the contents of one Amino Acid Reagent Powder Pillow for 1 mL of Amino Acid Reagent Solution.*

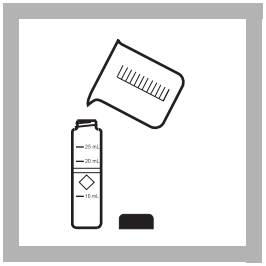


6. Press:

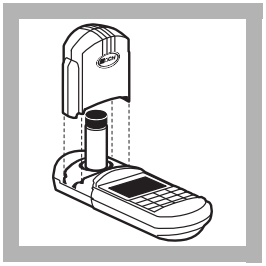
TIMER ENTER

A 10-minute reaction period will begin.

Note: *Perform Step 7 while the timer is running.*



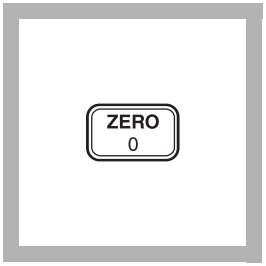
7. Pour 25 mL of sample (the blank) into a sample cell.



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

mg/L PO4

Place the blank into the cell holder. Cover the sample cell with the instrument cap.

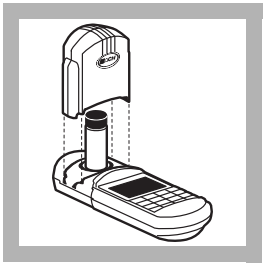


9. Press: **ZERO**

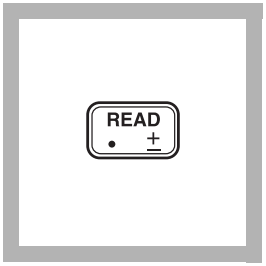
The cursor will move to the right, then the display will show:

0.0 mg/L PO4

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



10. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L PO_4 will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in clean plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use a commercial detergent containing phosphate for cleaning glassware used in this test.

Analyze samples immediately for best results. If prompt analysis is not possible, preserve samples by filtering immediately and storing the sample at 4 °C (39 °F) for up to 48 hours.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Phosphate PourRite Ampule Standard Solution, 500 mg/L as PO_4^{3-}.

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 well.

c) Analyze each sample as described in the procedure. Each 0.1-mL addition of standard should cause an increase of 2.0 mg/L orthophosphate (PO_4^{3-}).

d) If these increases do not occur, see *Standard Additions* (*Section 1*) for more information.

Standard Solution Method

Prepare a 10.0-mg/L phosphate standard by pipetting 10.0 mL of a Phosphate Standard Solution, 50 mg/L as PO_4^{3-} into a 50-mL volumetric flask. Dilute to volume with deionized water.

Or, prepare a 10.0-mg/L PO_4^{3-} standard solution by using the TenSette Pipet to add 1.00 mL of Phosphate PourRite Ampule Standard,
500 mg/L as PO_4^{3-}, into a 50-mL volumetric flask. Dilute to volume
with deionized water.

Substitute this standard for the sample and perform the test as described. The mg/L PO_4^{3-} reading should be 10 mg/L.

Method Performance

Precision

In a single laboratory using a standard solution of 15.0 mg/L PO_4^{3-} and two lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.12 mg/L PO_4^{3-}.

Estimated Detection Limit

The estimated detection limit for program 85 is 0.14 mg/L PO_4^{3-}. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Calcium (Ca^{2+})	Greater than 10,000 mg/L as $CaCO_3$
Chloride	Greater than 150,000 mg/L as Cl^-
Colored samples	Add 1 mL of 10 N Sulfuric Acid Standard Solution to another 25-mL sample. Use this instead of untreated sample as the blank to zero the instrument. Use a pipet and pipet filler to measure the sulfuric acid standard.
High salt levels (Na^+)	May cause low results. To eliminate this interference, dilute the sample until two successive dilutions yield about the same result.
Magnesium	Greater than 40,000 mg/L as $CaCO_3$
Nitrites (NO_2^-)	Bleach the blue color. Remove nitrite interference by adding 0.05 g of sulfamic acid to the sample. Swirl to mix. Continue with Step 4.
Phosphates, high levels (PO_4^{3-})	As the concentration of phosphate increases, the color changes from blue to green, then to yellow and finally to brown. The brown color may suggest a concentration as high as 100,000 mg/L PO_4^{3-}. If a color other than blue is formed, dilute the sample and retest.
Sulfide (S^{2-})	Sulfide interferes. For samples with sulfide concentration less than 5 mg/L, sulfide interference may be removed by oxidation with Bromine Water as follows: **1.** Measure 50mL of sample into a 125-mL flask. **2.** Add Bromine Water dropwise with constant swirling until permanent yellow color develops. **3.** Add Phenol Solution dropwise until the yellow color just disappears. Use this sample in Steps 3 and 7.
Temperature	For best results, sample temperature should be 21 ±3 °C (70 ±5 °F).
Turbidity	May give inconsistent results for two reasons. Some suspended particles may dissolve because of the acid used in the test. Also, desorption of orthophosphate from particles may occur. For highly turbid samples, add 1 mL of 10 N Sulfuric Acid Standard Solution to another 25-mL sample. Use this instead of untreated sample as the blank to zero the instrument. Use a pipet and pipet filler to measure the sulfuric acid standard.
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment.

Summary of Method

In a highly acidic solution, ammonium molybdate reacts with orthophosphate to form molybdophosphoric acid. This complex is then reduced by the amino acid reagent to yield an intensely colored molybdenum blue compound.

REQUIRED REAGENTS

	Cat. No.
High Range Reactive Phosphorus Reagent Set (100 Test)	22441-00

Includes: (1) 1934-32, (1) 2236-32

Description	Quantity Required Per Test	Units	Cat. No.
Amino Acid Reagent	1 mL	100 mL MDB*	1934-32
Molybdate Reagent	1 mL	100 mL MDB*	2236-32

REQUIRED APPARATUS

Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Description	Units	Cat. No.
Amino Acid Reagent Powder Pillow	100/pkg	804-99
Bromine Water, 30 g/L	29 mL	2211-20
Hydrochloric Acid Solution, 1:1 (6 N)	500 mL	884-49
Phenol Solution, 30 g/L	29 mL	2112-20
Phosphate Standard Solution, 50 mg/L PO_4^{3-}	500 mL	171-49
Phosphate Standard Solution, PourRite ampule, 500 mg/L PO_4^{3-}, 2 mL	20/pkg	14242-20
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sulfamic Acid	113 g	2344-14
Sulfuric Acid Standard Solution, 10 N	1 L	931-53
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28331-49
Water, deionized	4 L	272-56

* Larger sizes available.

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker Kit, PourRite	each	24846-00
Aspirator, vacuum	each	2131-00
Cylinder, graduated, 50 mL	each	508-41
Cylinder, graduated, mixing, 25 mL	each	20886-40
Filter Holder, 47 mm, 300 mL, graduated	each	13529-00
Filter, membrane, 47 mm, 0.45 microns	100/pkg	13530-00
Flask, filtering, 500 mL	each	546-49
Flask, erlenmeyer, 125 mL	each	505-43
Flask, volumetric, Class A, 50 mL	each	14574-41
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sens**ion***™*1*, portable with electrode	each	51700-10
Pipet, serological, 2.0 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 Tips, for 19700-01	1000/pkg	21856-28
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pipet Filler, safety bulb	each	12189-00
Spoon, measuring, 0.05 g	each	492-00
Thermometer, -20 to 110 °C, Non-Mercury	each	26357-02

For Technical Assistance, Price and Ordering

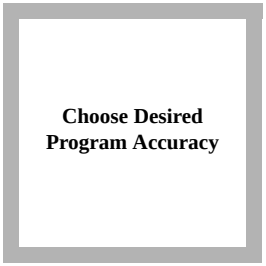
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

SULFATE (0 to 70 mg/L)

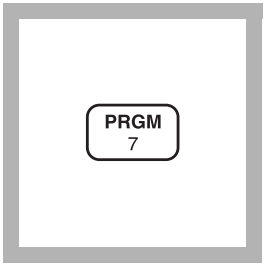
SulfaVer 4 Method* (Powder Pillows or AccuVac Ampuls); USEPA accepted for reporting wastewater analysis**

Using Powder Pillows



1. A User-Entered Calibration is necessary to obtain the most accurate results. See the *User Calibration* section at the back of this procedure. Program 91 can be used for process control or applications where a high degree of accuracy is not needed.

Note: *The nature of turbidimetric tests and reagent lot variation requires user calibration for best results.*

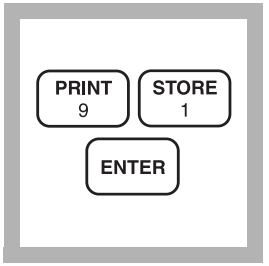


2. Enter the stored program number for sulfate (SO_4^{-}).

Press: **PRGM**

The display will show:

PRGM ?



3. Press: **91 ENTER** or the program number selected for a user-entered calibration.

The display will show **mg/L, SO4** and the **ZERO** icon.

4. Fill a clean sample cell with 10 mL of sample.

Note: *Filter highly turbid or colored samples. Use filtered sample in this step and as the blank.*

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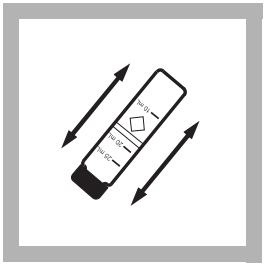
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

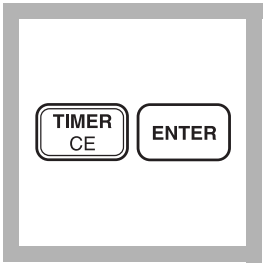
** Procedure is equivalent to USEPA method 375.4 for wastewater.



5. Add the contents of one SulfaVer 4 Sulfate Reagent Powder Pillow to the sample cell (the prepared sample). Cap the cell and invert several times to mix.

Note: *A white turbidity will develop if sulfate is present in the sample.*

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

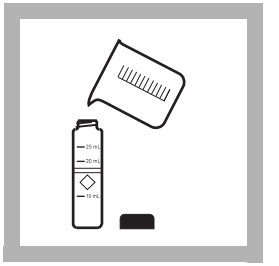


6. Press:

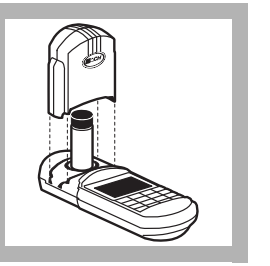
TIMER ENTER

A 5-minute reaction period will begin.

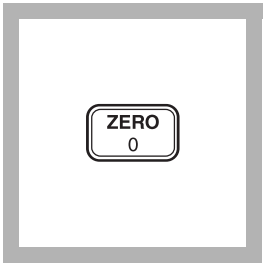
Allow the cell to stand undisturbed.



7. After the timer beeps, fill a second sample cell with 10 mL of sample (the blank).



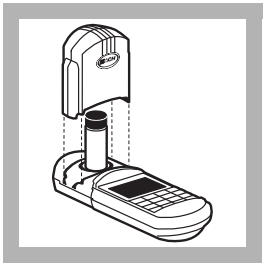
8. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



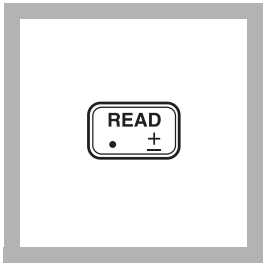
9. Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L SO4



10. Within five minutes after the timer beeps, place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



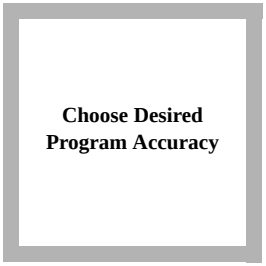
11. Press: **READ**

The cursor will move to the right, then the result in mg/L sulfate will be displayed.

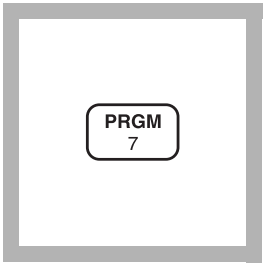
Note: *If Program 91 is used, use of the Standard Adjust is highly recommended. See Accuracy Check.*

Note: *Clean the sample cells with soap and a brush.*

Using AccuVac Ampuls



1. A User-Entered Calibration is necessary to obtain the most accurate results. See User Calibration Section at the back of this procedure. Program 92 can be used for process control or applications where a high degree of accuracy is not needed.

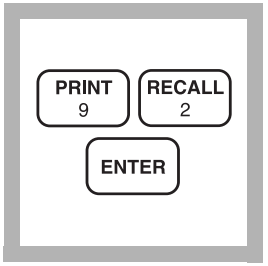


2. Enter the stored program number for sulfate (SO_4^-)-AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

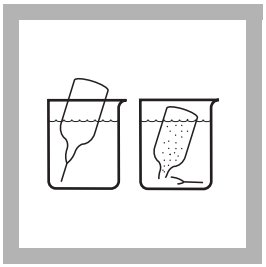


3. Press: **92 ENTER**

The display will show **mg/L, SO4** and the **ZERO** icon**.**

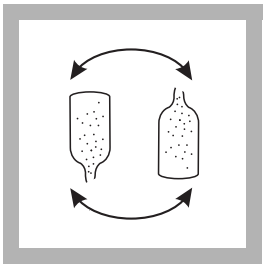
4. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

Note: *Filter highly turbid or colored samples. Use filtered sample in this step and as the blank.*



5. Fill a SulfaVer 4 Sulfate AccuVac Ampul with sample.

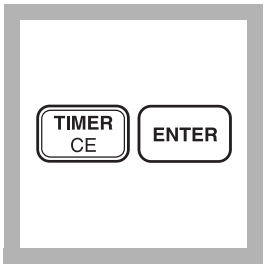
Note: *Keep tip immersed until the ampul fills completely.*



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

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

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

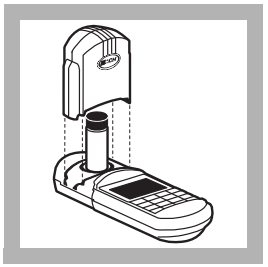


7. Press:

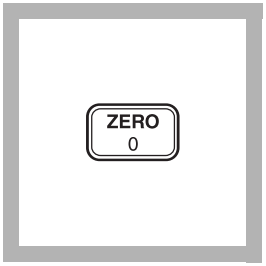
TIMER ENTER

A 5-minute reaction period will begin.

Note: *Allow the ampul to stand undisturbed.*



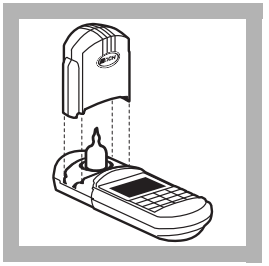
8. After the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



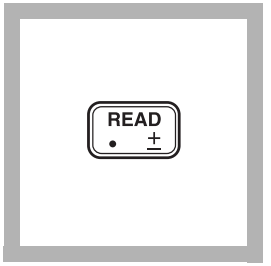
9. Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L SO4



10. Within five minutes after the timer beeps, place the AccuVac ampul into the cell holder. Tightly cover the sample cell with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L sulfate will be displayed.

Note: *If Program 92 is used, use of the Standard Adjust is highly recommended. See Accuracy Check.*

User- Entered Calibration

There are various programs to determine sulfate, each with a different level of accuracy. Best results are obtained by performing a user-entered calibration with each new lot of reagent. Programs 91 and 92 can be run when a high degree of accuracy is not needed. Use of the Standard Adjust feature will improve performance when using programs 91 and 92. It should NOT be used with a user calibration, as it will hinder performance.

Using Class A glassware, prepare standards of 10, 20, 30, 40, 50, 60, and 70 mg/L sulfate by pipetting 1, 2, 3, 4, 5, 6, and 7 mL of a 1000-mg/L sulfate standard into 100-mL volumetric flasks. Dilute to the mark with deionized water and mix well.

Zero the instrument with water. The user-entered settings for sulfate are:

Program number: #101 to 105
Wavelength: 520 nm
Resolution: 0 mg/L

See *Creating User-Entered Program* in the instrument manual for specific instructions on entering a user-entered program.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Samples may be stored up to 28 days by cooling to 4 °C (39 °F) or lower. Warm to room temperature before analysis.

Accuracy Check

Standard Additions Method- Powder Pillows

a) Snap the neck off a Sulfate Standard PourRite Ampule, 1000 mg/L SO_4^{2-} .

b) Use a TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard to the three 10-mL samples. Mix thoroughly.

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

d) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Additions Method- AccuVac Ampuls

a) Snap the neck off a Sulfate Standard PourRite Ampule, 2500 mg/L SO_4^{2-} .

b) Fill three 25- mL graduated cylinders with 25 mL of sample. Use a TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard to the three cylinders. Mix thoroughly. For AccuVac Ampuls, transfer to a 50-mL beaker.

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

d) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

Check the accuracy of the test by using the Sulfate Standard Solution, 50 mg/L, listed under Optional Reagents. Or, prepare this solution by pipetting 1.0 mL of a PourRite Ampule Standard for Sulfate (2500 mg/L) into a 50-mL volumetric flask. Dilute to volume with deionized water. The final concentration is 50 mg/L sulfate. Substitute this standard for the sample and proceed with the test as described in the procedure.

Standard Adjust
Standard adjust is recommended when using stored programs 91 or 92. It **should not** be used with a user-entered calibration.

To adjust the calibration curve using the reading obtained with the
50-mg/L standard solution, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **50** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment. See *Section 1, Standard Curve Adjustmen*t for more information.

Method Performance

Precision
In a single laboratory, using a standard solution of 50 mg/L sulfate and two representative lots of powder pillows with the instrument, a single operator obtained a standard deviation of ±0.5 mg/L sulfate.

In a single laboratory, using a standard solution of 50 mg/L sulfate and two representative lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation of ±3 mg/L sulfate.

Estimated Detection Limit (EDL)
The EDL for program 91 is 4.9 mg/L SO_4 and the EDL for program 92 is 3 mg/L SO_4. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

The following interfere at levels above those concentrations listed:

Calcium: 20,000 mg/L as $CaCO_3$	Magnesium: 10,000 mg/L as $CaCO_3$
Chloride: 40,000 mg/L as Cl^-	Silica: 500 mg/L as $CaCO_3$

Summary of Method

Sulfate ions in the sample react with barium in the SulfaVer 4 Sulfate Reagent to form insoluble barium sulfate. The amount of turbidity formed is proportional to the sulfate concentration. The SulfaVer 4 also contains a stabilizing agent to hold the precipitate in suspension.

REQUIRED REAGENTS AND APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Units	Cat. No.
SulfaVer 4 Sulfate Reagent Powder Pillows	1 pillow	100/pkg	21067-69
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

REQUIRED REAGENTS AND APPARATUS (Using AccuVac Ampuls)

SulfaVer 4 Sulfate AccuVac Ampuls	1 ampul	25/pkg	25090-25
Beaker, 50-mL	1	each	500-41H

OPTIONAL REAGENTS

Standard, Drinking Water Inorganics, F^-, NO_3^{-N}, PO_4^{-3}, SO_4^{-2}		500 mL	28330-49
Standard, Wastewater Effluent Inorganics, NH_3^{-N}, NO_3^{-N}, PO_4^{-3}, COD, SO_4^{-2}, TOC		500 mL	28332-49
Sulfate Standard Solution, 50 mg/L		500 mL	2578-49
Sulfate Standard Solution, 1000 mg/L		500 mL	21757-49
Sulfate Standard Solution, PourRite Ampule, 2500 mg/L, 10 mL		16/pkg	14252-10
Sulfate Standard Solution, PourRite Ampule, 1000 mg/L, 2 mL		20/pkg	21757-20
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit		each	24052-00
Cylinder, graduated mixing, 25 mL		each	20886-40
Filter Paper, folded, 12.5 cm		100/pkg	1894-57
Flask, volumetric, 50 mL, Class A		each	14574-41
Funnel, poly, 65 mm		each	1083-67
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 Pipet		50/pkg	21856-96
Pipet, volumetric, 1.00 mL, Class A		each	14515-35
Pipet, volumetric, 2.00 mL, Class A		each	14515-36
Pipet, volumetric, 3.00 mL, Class A		each	14515-03
Pipet, volumetric, 4.00 mL, Class A		each	14515-04
Pipet, volumetric, 5.00 mL, Class A		each	14515-37
Pipet, volumetric, 6.00 mL, Class A		each	14515-06
Pipet, volumetric, 7.00 mL, Class A		each	14515-07
Pipet Filler, safety bulb		each	14651-00
PourRite Ampule Breaker		each	24846-00

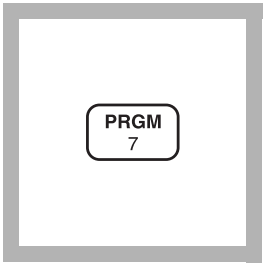
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

TURBIDITY (0 to 1000 FAU)

Absorptometric Method*



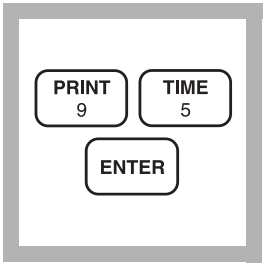
1. Enter the stored program number for turbidity.

Press: **PRGM**

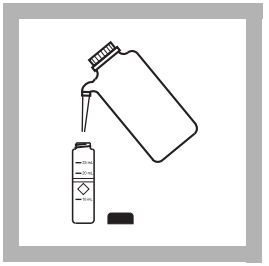
The display will show:

PRGM ?

Note:
1 FAU=1 NTU=1 FTU when measuring formazin. These are not equivalent when measuring other types of standards or samples.



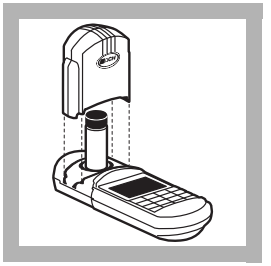
2. Press: **95 ENTER**
The display will show **FAU** and the **ZERO** icon.



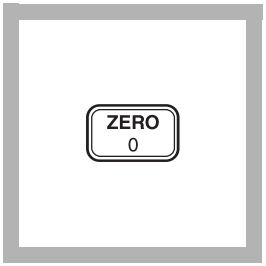
3. Fill a sample cell with 10 mL of deionized water (the blank).

Note: *Wipe the surface of the cell with a soft cloth.*

Note: *For highly colored samples, use a filtered portion of sample in place of the deionized water.*



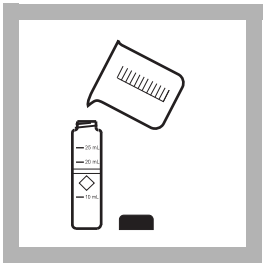
4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



5. Press: **ZERO**

The cursor will move to the right, then the display will show:

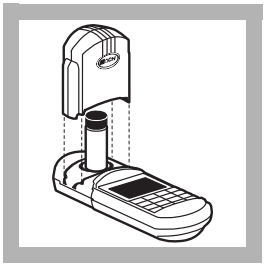
0 FAU



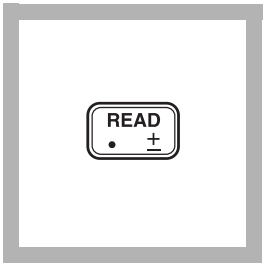
6. Fill another sample cell with 10 mL of sample.

Note: *Mix the sample well before transferring it to the sample cell.*

Note: *Wipe the surface of the cell with a soft cloth.*



7. Place the sample cell into the cell holder. Tightly cover the sample cell with the instrument cap.



8. Press: **READ**

The cursor will move to the right, then the result in Formazin Attenuation Units (FAU) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section I).*

* Adapted from FWPCA *Methods for Chemical Analysis of Water and Wastes*, 275 (1969)

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze samples as soon as possible. Store samples up to 48 hours by cooling to 4 °C (39 °F). Analyze the sample at the same temperature as it was collected.

Accuracy Check

Standard Solution Method

The stored program has been calibrated using formazin, the primary standard for turbidity. A 200 FAU formazin solution for checking the accuracy of the test can be prepared using the following procedure.

1. Pipet 5.00 mL of a 4000 NTU Formazin stock solution into a 100-mL volumetric flask.

2. Dilute to the mark with deionized water. Prepare this daily.

Convenient stabilized turbidity stock solution (200 NTU StablCal™ Standard) is available from Hach.

Standard Adjust

To adjust the calibration curve using the reading obtained with the
200 FAU formazin standard, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **200** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment. See *Section 1, Standard Curve Adjustment* for more information.

Method Precision

Precision

In a single laboratory, using a turbidity standard solution of 200 FAU with the instrument, a single operator obtained a standard deviation of ±2 FAU.

Estimated Detection Limit

The estimated detection limit for program 95 is 21 FAU. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Air Bubbles	Interfere at all levels. Degass samples using the Degassing Kit or an ultrasonic bath.
Color	Interferes if the color absorbs light at 520 nm.
Temperature extremes	May interfere by changing the turbidity of the sample. Analyze samples as soon as possible after collection. Analyze at the same temperature as the original sample.

Summary of Method

This turbidity test measures an optical property of the sample which results from scattering and absorption of light by particles in the sample. The amount of turbidity measured depends on variables such as the size, shape, color, and refractive properties of the particles.

This procedure is calibrated using formazin turbidity standards and the readings are in terms of Formazin Attenuation Units (FAU). This test cannot be used for USEPA reporting purposes, but it may be used for daily in-plant monitoring. One FAU is equivalent to one Nephelometric Turbidity Unit (NTU) of Formazin. However, the optical method of measurement for FAU is very different than the NTU method (1 NTU = 1 FTU = 1 FAU when traced to formazin primary standards.)

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

REQUIRED REAGENTS

Description	Units	Cat. No.
Formazin Stock Solution, 4000 NTU	500 mL	2461-49
Silicone Oil	15 mL DB	1269-36
StablCal Stabilized Turbidity Standard, 200 NTU	500 mL	26604-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Units	Cat. No.
Bath, ultrasonic	each	24895-00
Bottle, wash, 250 mL	each	620-31
Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, filter, 500 mL	each	546-49
Filter Holder	each	13529-00
Filter Pump, aspirator	each	2131-00
Oiling cloth, for applying silicone oil	each	26873-00
Pipet Filler, safety bulb	each	14651-00
Pipet, volumetric, Class A, 5.0 mL	each	14515-37
Sample Degassing Kit	each	43975-00
Stopper, rubber, one-hole, No. 7	6/pkg	2119-07
Tubing, rubber, 5/16” I.D.	12 feet	560-19
Tweezers, plastic	each	14282-00

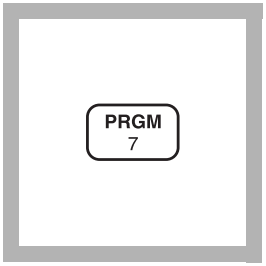
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

VOLATILE ACIDS (0 to 2800 as mg/L HOAc)

Esterification Method*



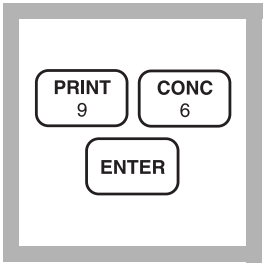
1. Enter the stored program number for Volatile Acids as acetic acid (HOAc).

Press: **PRGM**

The display will show:

PRGM ?

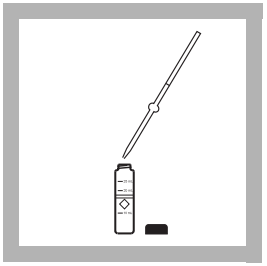
Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **96 ENTER**

The display will show **mg/L, HOAc** and the **ZERO** icon**.**

Note: *If high levels of dissolved solids or mineral acids are present, distill as described in the Hach Distillation Apparatus manual.*



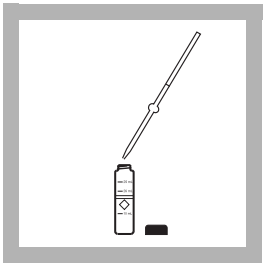
3. Pipet 0.5 mL of deionized water into a dry 25-mL sample cell (the blank).

Note: *Use a Class A or TenSette Pipet.*

Note: *Adjust the pH of stored samples before analysis.*

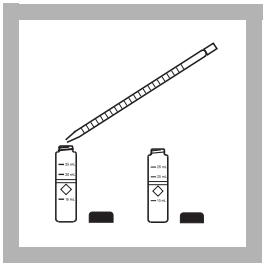
4. Filter or centrifuge 25 mL of the sample.

Note: *Centrifugation is faster than filtration.*

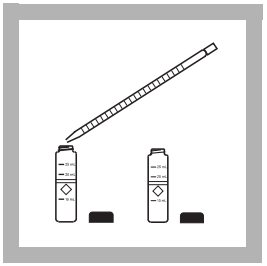


5. Pipet 0.5 mL of the filtrate or supernatant into another dry 25-mL sample cell (the prepared sample).

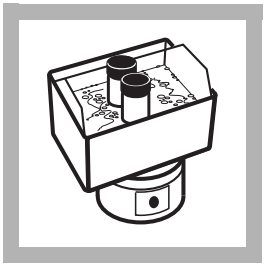
Note: *Use a Class A or TenSette Pipet.*



6. Pipet 1.5 mL of ethylene glycol into each sample cell. Swirl to mix.



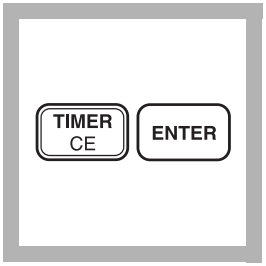
7. Pipet 0.2 mL of 19.2 N Sulfuric Acid Standard Solution into each cell. Swirl to mix.



8. Place both cells into a boiling water bath.

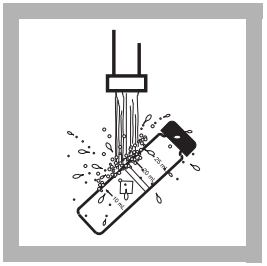
Note: *Samples may be boiled in a 600-mL beaker.*

* Adapted from *The Analyst*, 87, 949 (1962)

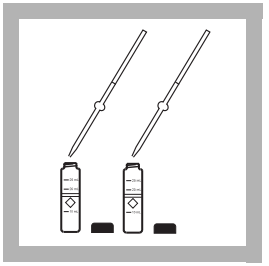


9. Press: **TIMER ENTER**

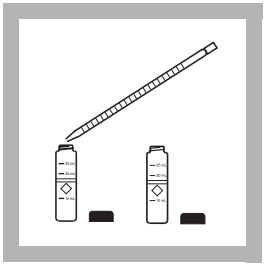
A 3-minute reaction period will begin.



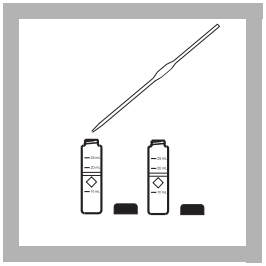
10. When the timer beeps, cool solutions to 25 °C (until cells feel cool) with running tap water. Then dry the cells with a soft cloth.



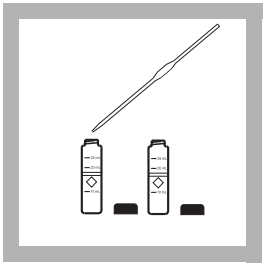
11. Pipet 0.5 mL of Hydroxylamine Hydrochloride Solution into each cell. Swirl to mix.



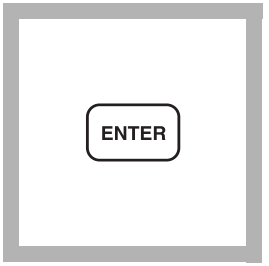
12. Pipet 2.0 mL of 4.5 N Sodium Hydroxide Standard Solution into each cell. Cap and invert to mix.



13. Add 10 mL of Ferric Chloride Sulfuric Acid Solution to each cell. Cap and invert to mix.



14. Add 10 mL of deionized water to each cell. Cap and invert to mix.

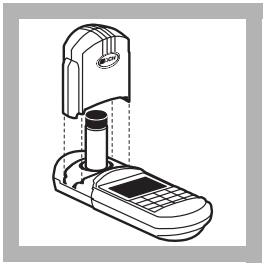


15. The display will show: **3:00 TIMER 2**

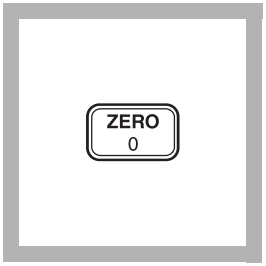
Press: **ENTER**

A 3-minute reaction period will begin.

Note: *After this three-minute reaction period, proceed immediately through steps 16-19.*



16. When the timer beeps, immediately place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

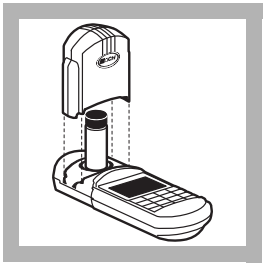


17. Press: **ZERO**

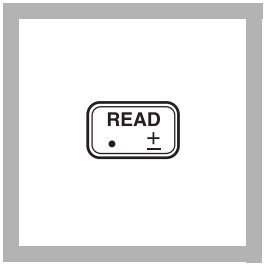
The cursor will move to the right, then the display will show:

0 mg/L HOAc

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



18. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



19. Press: **READ**

The cursor will move to the right, then the result in mg/L Volatile Acids as acetic acid will be displayed.

Sampling and Storage

Collect samples in plastic or glass bottles. Analyze samples as soon as possible after collection. Samples can be stored up to 24 hours by cooling to 4 °C (39 °F) or below. Warm to room temperature before testing.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Volatile Acids PourRite Ampule Standard Solution, 62,500 mg/L as acetic acid.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard, respectively, to three 25-mL graduated mixing cylinders, each containing 25 mL of filtered sample. Stopper. Shake well to mix.

c) Remove a 0.5 mL aliquot of sample from each cylinder; add to three dry sample cells. Analyze all three samples along with the original test sample beginning with Step 5 of the procedure. The volatile acid concentration should increase 250 mg/L volatile acids as acetic acid for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section 1.*

Standard Solution Method

Prepare a 500 mg/L volatile acid standard by using the TenSette Pipet to add 0.8 mL of a Volatile Acids PourRite Ampule Standard Solution (62,500 mg/L as acetic acid) to a 100-mL volumetric flask. Dilute to volume with deionized water. Stopper and invert to mix.

Method Performance

Precision

In a single laboratory, using a standard solution of 500 mg/L volatile acids as acetic acid and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±8 mg/L.

Estimated Detection Limit

The estimated detection limit for program 96 is 17 mg/L HOAc. For more information on the estimated detection limit, see *Section 1*.

Summary of Method

The volatile acids test is designed specifically for the determination of volatile acids in digestor sludges. The method is based on esterification of the carboxylic acids present and determination of the esters by the ferric hydroxamate reaction. All volatile organic acids present are reported as their equivalent mg/L acetic acid.

REQUIRED REAGENTS

	Cat. No.
Volatile Acids Reagent Set (90 tests)	22447-00
Includes: (1) 2039-53, (2) 2042-53, (1) 818-42, (1) 2040-53, (1) 2038-32	

Description	Quantity Required Per Test	Units	Cat. No.
Ethylene Glycol	3 mL	1000 mL	2039-53
Ferric Chloride-Sulfuric Acid Solution	20 mL	1000 mL	2042-53
Hydroxylamine Hydrochloride Solution, 100 g/L	1 mL	100 mL	818-42
Sodium Hydroxide Standard Solution, 4.5 N	4 mL	1000 mL	2040-53
Sulfuric Acid Standard Solution, 19.2 N	0.4 mL	100 mL	2038-32
Water, deionized	20.5 mL	4 L	272-56

REQUIRED APPARATUS

Description	Quantity Required Per Test	Units	Cat. No.
Cots, finger	2	2/pkg	14647-02
Cylinder, graduated, 10 mL	1	each	508-38
Filter Paper, folded, 12.5 cm	1	100/pkg	1894-57
Flask, erlenmeyer, 50 mL	1	each	505-41
Funnel, poly, 65 mm	1	each	1083-67
Hot Plate, circular, 3.5-inch diameter	1	each	12067-01
Pipet Filler, safety bulb	1	each	14651-00
Pipet, serological, 2 mL	2	each	532-36
Pipet, volumetric, Class A, 0.5 mL	3	each	14515-34
Pipet, volumetric, Class A, 10.00 mL	3	each	14515-38
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06
Water Bath and Rack	1	each	1955-55

OPTIONAL REAGENTS

Volatile Acids Standard Solution, PourRite ampule, 62,500 mg/L as acetic acid, 10 mL		16/pkg	14270-10

OPTIONAL APPARATUS

Ampule Breaker, PourRite		each	24846-00
Beaker, 600 mL		each	500-52
Bottle, wash, 500 mL		each	620-11
Centrifuge, laboratory, 115 Vac		each	26765-00
Centrifuge, laboratory, 230 Vac		each	26765-02
Centrifuge Tubes, 15 mL		10/pkg	22787-39
Centrifuge Tube Caps		20/pkg	25852-20
Cylinder, graduated, mixing, 25 mL		each	1896-40
Cylinder, graduated, plastic, 250 mL		each	1081-46
Distillation Apparatus		each	22653-00
Distillation Heater and Support Apparatus		each	22744-00
Flask, volumetric, Class A, 100 mL		each	14574-42
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
Pipet, TenSette, 1.0 to 10.0 mL		each	19700-10
Pipet Tips, for 19700-10		50/pkg	21997-96

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

SECTION 5 ORDERING INFORMATION

By Phone:
6:30 a.m. to 5:00 p.m. MST
Monday through Friday
800-227-HACH (800-227-4224)

By Mail:
Hach Company
P. O. Box 389
Loveland, Colorado 80539-0389 U.S.A.

By FAX:
970-669-2932 (Hach Loveland)

Information Required:

- Hach account number (if available)
- Billing address
- Shipping address
- Your name and phone number
- Purchase order number
- Catalog number
- Brief description or model number
- Quantity

Technical and Customer Service

Hach Technical and Customer Service Department personnel are eager to answer questions about our products and their use and to take your orders. Specialists in analytical methods, they are happy to put their talents to work for you. Call **1-800-227-4224**.

International Customers

Hach maintains a network of dealers and distributors throughout the world.

In Canada
Hach Sales and Service Canada Ltd.
1313 Border Street, Unit 34
Winnipeg, Manitoba R3H 0X4
Telephone: (204) 632-5598
FAX: (204) 694-5134

In other countries, contact:
Hach Company World Headquarters
P. O. Box 389
Loveland, Colorado, U.S.A. 80539-0389
Telephone: (1) (970) 669-3050
FAX: (1) (970) 669-2932

Information presented on these pages applies only to Hach products manufactured for use within the United States. Exportation of these products renders these terms void.

Prices and Terms

Prices are subject to change without notice. All prices are FOB from the shipping point (usually Ames, Iowa). Hach offers instant credit up to $200 on Net 30 Day terms. Larger orders are subject to credit review. Customers may send remittance with orders or we can ship C.O.D. if you prefer.

Warranty

Hach warrants its products to be of high quality, to be free of material defects on the date of shipment and to be as specified.

Limits of Usage

Our chemicals and reagents are offered for laboratory and manufacturing use ONLY. They may not be used as drugs, cosmetics or food additives.

MSDS

Hach Material Safety Data Sheets, among the most complete and informative in the industry, provide comprehensive safety data essential for day-to-day operations and safety training.

An MSDS accompanies all Hach chemical products including test kits. For an additional cost, we will print MSDSs on your own forms.

ADDITIONAL INFORMATION

Label Information

Labels on Hach chemicals and reagents supply the following:

- Product Name -- In French, German, Italian and Spanish as well as English is printed on all but the smallest-size labels.
- Hach Catalog Number -- Makes reordering easy and helps match the appropriate MSDS.
- Storage Information and Lot Numbers -- Lot numbers made up of letters and numbers indicate an extended shelf life; a four-digit number indicates items should be rotated and checked with a standard to confirm performance. The lot number is essential if you call for technical assistance or with questions about reagent performance.

Shipping

Our experienced warehouse staff packages your orders for safe arrival. Unless we are instructed otherwise, the best and most efficient mode of transportation is selected. Motor freight shipments will be sent freight collect unless you specify otherwise at the time you order.

If you have questions about methods for shipment and availability of special packaging, please ask when you place your order.

Claims and Returns

We take extreme care to fill, check, re-check and pack orders properly. If errors or damages should occur, please report details to our Loveland Customer Service Department and to the carrier immediately. Be sure to keep all containers and packing materials.

AUTHORIZATION MUST BE OBTAINED from Hach when returning items for any reason. Call 1-800-227-4224 toll free. **ALL "FREIGHT COLLECT" SHIPMENTS OR MERCHANDISE RETURNED WITHOUT PROPER AUTHORIZATION FROM HACH WILL BE REFUSED.**

MAIL ORDER FORM

Send order to: HACH COMPANY, P.O. Box 608, Loveland, CO 80539-0608

Use this convenient form, your own purchase orders, or for PROMPT PHONE SERVICE CALL 1-800-227-4224. If ordering by phone, please have information related to items 1 - 4 (below) ready.

☐ Check box if "Ship To" information is identical to "Bill To".

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OF

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CITY **STATE** **ZIP**

ATTENTION

HACH ACCOUNT NO. (If available) ❶

PAYMENT METHOD: ☐ **Check** ☐ **MasterCard** ☐ **Visa** ☐ **Purchase Order**

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Card Account or Purchase Order No. Card Exp. Date Signature

❷ QUANTITY	❸ CAT. NO.	❹ DESCRIPTION	❺ UNIT SIZE	UNIT PRICE	TOTAL

❶ If Hach account number is not known, leave the space blank.

❷ Most chemicals and apparatus are sold separately ("each"), but others are sold in units. Powder pillows, for example, are available in packages of 100. To purchase 100 powder pillows, order 1 unit, not 100 pillows. Be sure to order the number of units (packages) you need.

❸ Include all numbers given in the products listing.

❹ A one- or two-word description of the item.

❺ If more than one size of an item is offered, state the size you want.

❻ Unless otherwise instructed, Hach will choose the best and most efficient mode of transportation and calculate the amount.

❼ Check one box. Tax exempt status must be substantiated with documentation identifying your tax exempt number. If taxable, sales tax will be added.

QUANTITY	CAT. NO.	DESCRIPTION	UNIT SIZE	UNIT PRICE	TOTAL
				❻ Shipping Charge	
				❼ TAXABLE? ☐ Yes ☐ No*	
				TOTAL ORDER	

Prices are subject to change without notice

*If no, tax exempt document is: ☐ Enclosed ☐ On file at Hach

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HACH ACCOUNT NO. (If available) ❶

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Card Account or Purchase Order No. Card Exp. Date Signature

❷ QUANTITY	❸ CAT. NO.	❹ DESCRIPTION	❺ UNIT SIZE	UNIT PRICE	TOTAL

_____

❶ If Hach account number is not known, leave the space blank.

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❹ A one- or two-word description of the item.

❺ If more than one size of an item is offered, state the size you want.

❻ Unless otherwise instructed, Hach will choose the best and most efficient mode of transportation and calculate the amount.

❼ Check one box. Tax exempt status must be substantiated with documentation identifying your tax exempt number. If taxable, sales tax will be added.

QUANTITY	CAT. NO.	DESCRIPTION	UNIT SIZE	UNIT PRICE	TOTAL
				❻ Shipping Charge	
				❼ TAXABLE? ☐ Yes ☐ No*	
				TOTAL ORDER	

Prices are subject to change without notice

*If no, tax exempt document is: ☐ Enclosed ☐ On file at Hach

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NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY MAIL

FIRST CLASS MAIL PERMIT NO. 100 LOVELAND, CO

POSTAGE WILL BE PAID BY ADDRESSE

HACH COMPANY—SALES DEPT.
P.O. Box 608
Loveland, CO 80539-0608

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