Method 8143

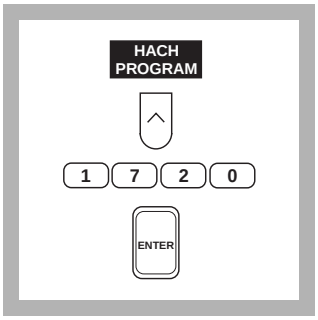
Porphyrin Method*

Powder Pillows

(0 to 210.0 µg/L)

Scope and Application: *For water, wastewater and seawater; digestion is required for determining total copper. See SECTION 2 for digestion procedure. The estimated detection limit for program number 1720 is 1.4 mg/L Cu.*

* Adapted from Ishii and Koh, *Bunseki Kagaku*, 28, 473 (1979)



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

Select the stored program for porphyrin copper by pressing **1720** with the numeric keys.

Press: **ENTER**

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

Note: *The Flow Cell and Sipper Modules can be used for this procedure. Use a 25-mL sample and reagents with the Flow Cell Module.*

2. The display will show:

HACH PROGRAM: 1720
Copper, Porphyrin

The wavelength (λ), **425 nm**, is automatically selected.

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

3. Fill two sample cells with 10 mL of sample.

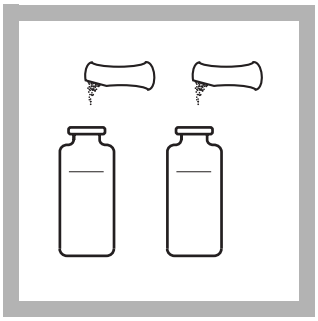
Note: *Wash all glassware with detergent. Rinse with tap water. Rinse again with 1:1 Nitric Acid Solution. Rinse a third time with copper-free, deionized water.*

Note: *For proof of accuracy, use a 150 µg/L copper standard solution (preparation given in the Accuracy Check* section*) in place of the sample.*

Note: *For non-preserved samples with extreme pH see Interferences section.*

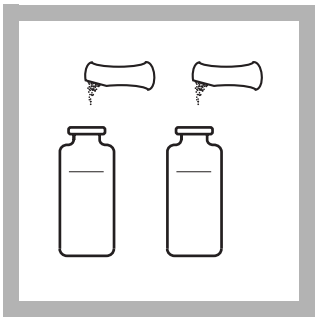
4. Add the contents of one Copper Masking Reagent Powder Pillow to one of the sample cells (the blank). Swirl to dissolve.

Note: *The sample cell without masking agent is the prepared sample.*



5. Add the contents of one Porphyrin 1 Reagent Powder Pillow to each sample cell.

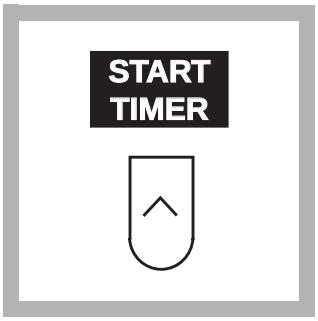
Swirl to dissolve.



6. Add the contents of one Porphyrin 2 Reagent Powder Pillow to each sample cell.

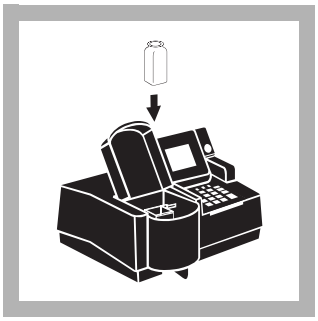
Swirl to dissolve.

Note: *The yellow color will turn blue momentarily. If any copper is present, the sample will return to yellow.*

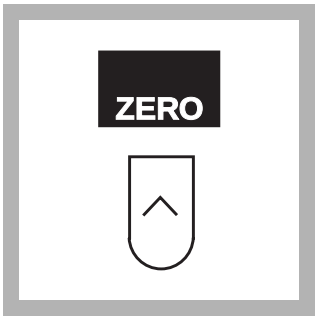


7. Press the soft key under ***START TIMER***.

A 3-minute reaction period will begin.



8. When the timer beeps, place the blank into the cell holder. Close the light shield.



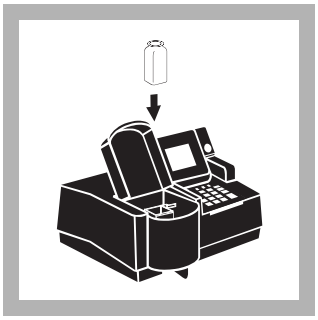
9. Press the soft key under ***ZERO***.

The display will show:

0.0 µg/L Cu

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

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



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

Note: *If samples with high levels of metal are analyzed, a slight metallic deposit or yellow buildup may appear on the sample cell wall. Remove by washing as recommended in Step 3.*

Interferences

The following may interfere when present in concentrations exceeding the levels listed below.

Table 1 Interfering Substances and Suggested Treatments

Interfering Substance	Interference Levels and Treatments
Aluminum, Al^{3+}	60 mg/L
Cadmium, Cd^{2+}	10 mg/L
Calcium, Ca^{2+}	1500 mg/L
Chelating agents	Interfere at all levels unless either the Digesdahl or vigorous digestion is performed (see Section *2*).
Chloride, Cl^{-}	90,000 mg/L
Chromium, Cr^{6+}	110 mg/L
Cobalt, Co^{2+}	100 mg/L
Fluoride, F^{-}	30,000 mg/L
Iron, Fe^{2+}	6 mg/L
Lead, Pb^{2+}	3 mg/L
Magnesium	10,000 mg/L
Manganese	140 mg/L
Mercury, Hg^{2+}	3 mg/L
Molybdenum	11 mg/L
Nickel, Ni^{2+}	60 mg/L
Potassium, K^{+}	60,000 mg/L
Sodium, Na^{+}	90,000 mg/L
Zinc, Zn^{2+}	9 mg/L
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment; (see Section *1.3.1 pH Interferences*.)

Sample Collection, Storage and Preservation

Collect samples in acid-washed plastic bottles. To preserve, adjust the pH to 2 or less with nitric acid (about 5 mL per liter). Store preserved samples up to six months at room temperature. Before testing, adjust the pH of the preserved sample to between 2 and 6. If the sample is too acidic, adjust the pH with 5.0 N Sodium Hydroxide Standard Solution. Correct test results for volume additions; see Section *1.2.2 Correcting for Volume Additions.*

Accuracy Check

Standard Additions Method

a. Prepare a 4000-µg/L copper standard by adding 4.00 mL Copper Standard Solution, 100.0-mg/L, to a 100-mL volumetric flask. Dilute to 100 mL with copper-free deionized water.

b. Leave the unspiked sample in the sample cell compartment. Verify that the units displayed are in µg/L. Select standard additions mode by pressing the soft keys under ***OPTIONS, (MORE***) and then ***STD ADD***.

c. Press **ENTER** to accept the default sample volume (mL), 10.

d. Press **ENTER** to accept the default standard concentration (µg/L), 4000.

e. Press the soft key under ***ENTRY DONE***.

f. Fill eight sample cells with 10 mL of sample. Use the TenSette Pipet to add 0.1 mL of Copper Standard Solution, 4000-µg/L Cu, to two of the sample cells. Then pipet 0.2 mL of the standard solution into two more cells. Finally, pipet 0.3 mL of the standard solution into two more cells.

g. Analyze each standard addition sample as described above, using one of the two spiked samples in each set as the blank. Accept the standard additions reading by pressing the soft key under **READ** each time. The copper concentration reading should reflect approximately 100% recovery.

h. After completing the sequence, the display will show the extrapolated concentration value and the "best-fit" line through the standard additions data points, accounting for matrix interferences.

i. See Section *1.4.1 Standard Additions* for more information.

Standard Solutions Method

To assure the accuracy of the test, prepare a 150-µg/L copper standard by pipetting 15.00 mL of Copper Standard Solution, 10.0-mg/L Cu, into a 1000-mL volumetric flask. Dilute to the mark with copper-free, reagent-grade water. Prepare this solution daily. Perform the copper procedure as described above.

To adjust the calibration curve using the reading obtained with the 150 µg/L standard solution, press the soft keys under ***OPTIONS, MORE*** then ***STD: OFF***. Press **ENTER** to accept the displayed concentration, the value of which depends on the selected units. If an alternate concentration is used, enter the actual concentration and press **ENTER** to return to the read screen. See Section *1.5.5 Adjusting the Standard Curve* for more information.

Method Performance

Precision

Standard: 150 µg/L Cu

Program	95% Confidence Limits
1720	149.2–150.8 µg/L Cu

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

Estimated Detection Limit

Program	EDL
1720	1.4 µg/L Cu

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

Sensitivity
Program Number: 1720

Portion of Curve:	∆Abs	∆Concentration
Entire Range	0.010	1.4 µg/L Cu

See Section *1.5.3 Sensitivity Explained* for more information.

Calibration Standard Preparation

To perform a copper calibration using the porphyrin method, prepare a 1000-µg/L copper stock solution by pipetting 10 mL of a 100-mg/L Copper Standard Solution (Cat. No. 128-42) into a 1000-mL volumetric flask using Class A glassware. Dilute to the mark with deionized water and mix thoroughly.

Prepare calibration standards containing 20.0, 40.0, 80.0, 120.0, 160.0, 200.0 and 240.0 µg/L Cu as follows:

a. Into seven different 100-mL Class A volumetric flasks, pipet 2.00, 4.00, 8.00, 12.00, 16.00, 20.00 and 24.00 mL of the 1000-µg/L Cu stock solution using Class A glassware.

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

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

Summary of Method

The porphyrin method is very sensitive to trace amounts of free copper. The method is free from most interferences and does not require any sample extraction or concentration before analysis. Interferences from other metals are eliminated by the copper masking reagent. The porphyrin indicator forms an intense, yellow-colored complex with any free copper present in sample.

Safety

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

Pollution Prevention and Waste Management

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

REQUIRED REAGENTS AND STANDARDS

	Cat. No.
Copper Reagent Set (100 Tests)	26033-00

Includes: (1) 26034-49, (2) 26035-49, (2) 26036-49

Description	Quantity Required per test	Unit	Cat. No.
Copper Masking Reagent Powder Pillows	1 pillow	100/pkg	26034-49
Porphyrin 1 Reagent Powder Pillows	2 pillows	100/pkg	26035-49
Porphyrin 2 Reagent Powder Pillows	2 pillows	100/pkg	26036-49

REQUIRED EQUIPMENT AND SUPPLIES

DR/4000 1-Inch Cell Adapter	1	each	48190-00

OPTIONAL REAGENTS AND STANDARDS

Copper Standard Solution, 100-mg/L Cu	100 mL	128-42
Copper Standard Solution, 10-mg/L Cu	100 mL	129-42
Hydrochloric Acid, 6 N	500 mL	884-49
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Sodium Hydroxide, 5 N	1 liter	2450-53
Sodium Hydroxide Standard Solution, 5 N	100 mL MDB	2450-32
Water, deionized	4 liters	272-56

OPTIONAL EQUIPMENT AND SUPPLIES

Beaker, 100-mL	each	500-42
Clipper, for opening powder pillows	each	968-00
DR/4000 Carousel Module Kit	each	48070-02
DR/4000 Flow Cell Module Kit, 1-inch	each	48070-04
DR/4000 Flow Cell Module Kit, 1-cm	each	48070-05
DR/4000 Sipper Module Kit, 1-inch	each	48090-03
Flask, volumetric, Class A, 100-mL	each	14574-42
Flask, volumetric, Class A, 1000-mL	each	14574-53
Hot Plate, 7 x 7 in., 120 VAC, 50/60 Hz	each	23441-00
Hot Plate, 7 x 7 in., 240 VAC, 50/60 Hz	each	23441-02
pH Paper, pH 1.0 to 11.0	5 rolls/pkg	391-33
pH Meter, *sens**ion***™*1*, portable	each	51700-00
Pipet, Mohr, 5-mL	each	20934-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01	50/pkg	21856-96
Pipet, volumetric, Class A, 2-mL	each	14515-36
Pipet, volumetric, Class A, 4-mL	each	14515-04
Pipet, volumetric, Class A, 6-mL	each	14515-06
Pipet, volumetric, Class A, 8-mL	each	14515-08
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet Filler, safety bulb	each	14651-00
Watch Glass, Pyrex, 100-mm	each	578-70

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