# Copper

DOC316.53.01038

## Porphyrin Method[1]

## Method 8143

## 1 to 210 µg/L Cu (LR)

## Powder Pillows

**Scope and application:** For water, wastewater and seawater.

[1] Adapted from Ishii and Koh, Bunseki Kagaku, 28 (473), 1979.

## Test preparation

### Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests.

To use the table, select an instrument, then read across to find the applicable information for this test.

**Table 1 Instrument-specific information**

| Instrument | Sample cell orientation | Sample cell |
|---|---|---|
| DR6000<br>DR3800<br>DR2800<br>DR2700<br>DR1900 | The fill line is to the right. | 2495402<br>  |
| DR5000<br>DR3900 | The fill line is toward the user. | |
| DR900 | The orientation mark is toward the user. | 2401906<br>  |

### Before starting

| |
|---|
| Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed. |
| To make sure that all forms of the metal are measured, digest the sample with heat and acid. Use the mild or vigorous digestion. Refer to the *Water Analysis Guide* for more information. |
| Wash all glassware with detergent. Rinse with tap water. Rinse again with 1:1 nitric acid solution. Rinse a third time with high-quality deionized water. These steps will remove deposits that can cause slightly high results. |
| If samples contain high levels of metals, a slight metallic deposit or yellow buildup may form in the sample cell. Wash the cell as described above. |
| For the best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to determine the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option. |
| Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment. |
| Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information. |

## Items to collect

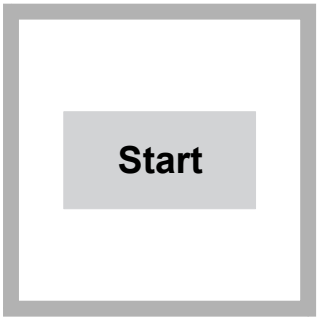
| Description | Quantity |
|---|---|
| Copper Masking Reagent Powder Pillows, 10-mL | 1 |
| Porphyrin 1 Reagent Powder Pillows, 10-mL | 2 |
| Porphyrin 2 Reagent Powder Pillows, 10-mL | 2 |
| Nitric Acid Solution, 1:1 | varies |
| Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.) | 2 |

Refer to Consumables and replacement items on page 5 for order information.

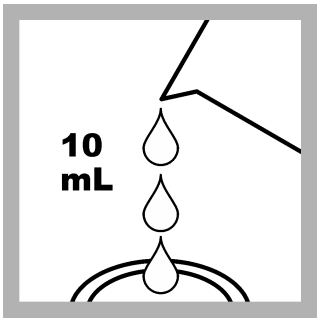
## Sample collection and storage

- Collect samples in clean glass or plastic bottles that have been cleaned with 6 N (1:1) hydrochloric acid and rinsed with deionized water.
- To preserve samples for later analysis, adjust the sample pH to less than 2 with concentrated nitric acid (approximately 2 mL per liter). No acid addition is necessary if the sample is tested immediately.
- Keep the preserved samples at room temperature for a maximum of 6 months.
- Before analysis, adjust the pH to 2–6 with 5 N sodium hydroxide solution.
- Correct the test result for the dilution caused by the volume additions.

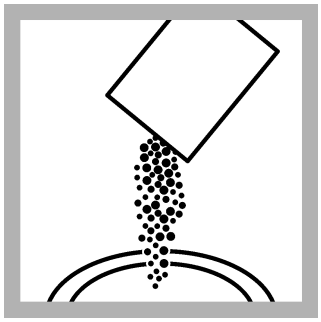
## Powder pillow procedure



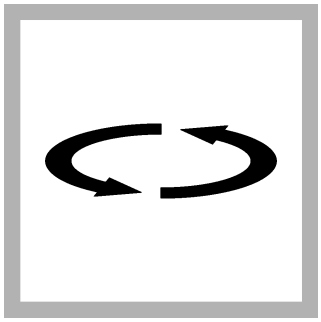

**1.** Start program **145 Copper, Porphyrin**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



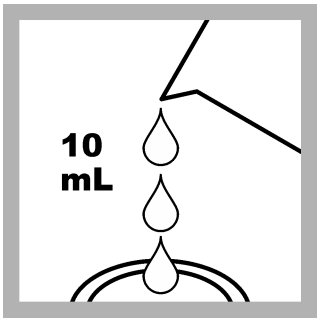

**2. Prepare the blank:** Fill the sample cell with 10 mL of sample.



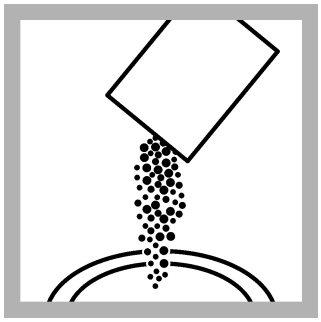
**3.** Add the contents of one Copper Masking Reagent powder pillow.



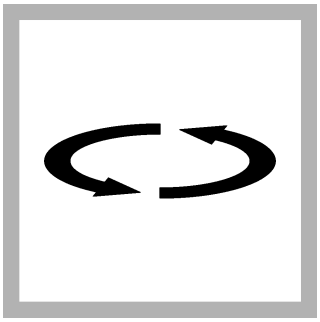
**4.** Swirl to dissolve the reagent.



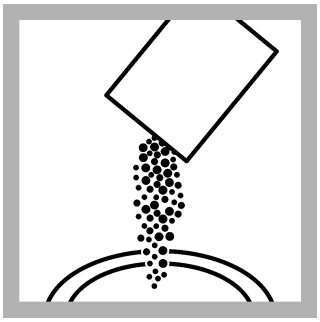

**5. Prepare the sample:** Fill a second sample cell with 10 mL of sample.



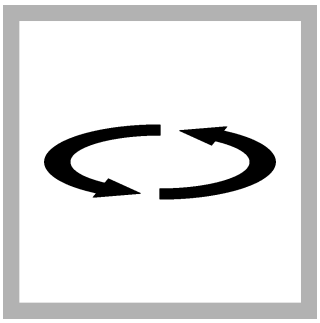
**6.** Add the contents of one Porphyrin 1 Reagent Powder Pillow to each sample cell.



**7.** Swirl to mix.

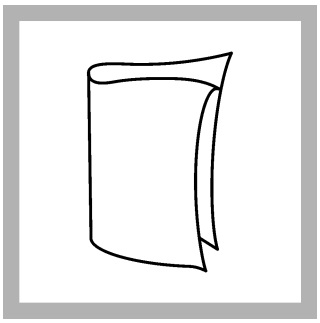


**8.** Add the contents of one Porphyrin 2 Reagent Powder Pillow to each sample cell.

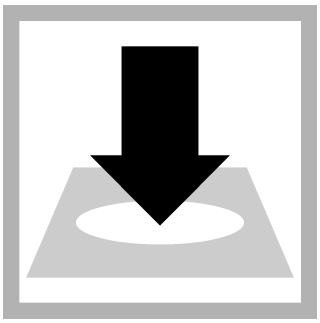


**9.** Swirl to mix.
If copper is present in the sample, the sample will show blue, then go back to a yellow color.

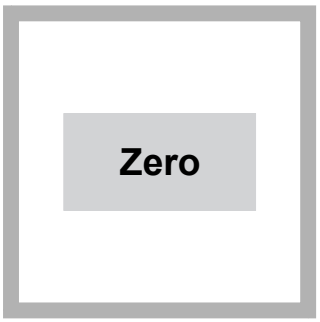

**10.** Start the instrument timer. A 3-minute reaction time starts.



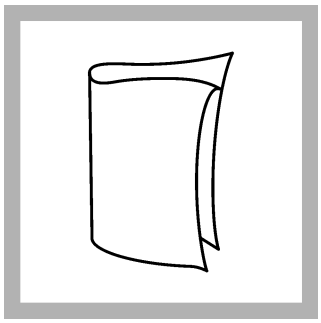
**11.** When the timer expires, clean the blank sample cell.



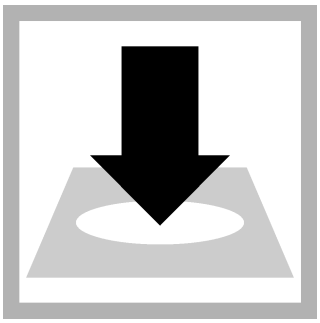
**12.** Insert the blank into the cell holder.




**13.** Push **ZERO**. The display shows 0 µg/L Cu.



**14.** Clean the prepared sample cell.



**15.** Insert the prepared sample into the cell holder.


**16.** Push **READ**. Results show in µg/L Cu.

## Interferences

| Interfering substance | Interference level |
|---|---|
| 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 the sample is pretreated with a vigorous digestion. |
| Chloride, $Cl^{-}$ | 90,000 mg/L |
| Chromium, $Cr^{6+}$ | 110 mg/L |

| Interfering substance | Interference level |
|---|---|
| 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 | Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary. |

## Accuracy check

### Standard additions method (sample spike)

Use the standard additions method (for applicable instruments) to validate the test procedure, reagents and instrument and to find if there is an interference in the sample.

Items to collect:

- Copper Standard Solution, 4 mg/L (PourRite® Ampule or prepare from a dilution of a higher concentration copper standard solution)
- Ampule breaker
- Pipet, TenSette®, 0.1–1.0 mL and tips

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare six spiked 10-mL samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to two 10-mL portions of fresh sample. Mix well.
6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   ***Note:*** *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

### Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

Items to collect:

- Copper Standard Solution, 10 mg/L
- 1000-mL volumetric flask, Class A
- Deionized water

1. Prepare a 150 µg/L copper standard solution as follows:
   a. Add 15.00 mL of 10-mg/L copper standard solution into the volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
2. Use the test procedure to measure the concentration of the prepared standard solution.
3. Compare the expected result to the actual result.

   ***Note:*** *The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are small variations in the reagents or instruments.*

## Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

| Program | Standard | Precision (95% confidence interval) | Sensitivity<br>Concentration change per 0.010 Abs change |
|---|---|---|---|
| 145 | 50 µg/L Cu | 47–53 µg/L Cu | 1 µg/L Cu |

## 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 most other metals are removed with the copper masking reagent. The porphyrin indicator forms an intense, yellow-colored complex with any free copper present in sample. The measurement wavelength is 425 nm for spectrophotometers or 420 nm for colorimeters.

## Consumables and replacement items

### Required reagents and apparatus

| Description | Quantity/test | Unit | Item no. |
|---|---|---|---|
| Nitric Acid Solution, 1:1 | varies | 500 mL | 254049 |
| Copper Reagent Set, Porphyrin, 10 mL | 1 | 100/pkg | 2603300 |
| Includes: | | | |
| Copper Masking Reagent Powder Pillow, 10 mL | 1 | 100/pkg | 2603449 |
| Porphyrin 1 Reagent Powder Pillow, 10 mL | 2 | 100/pkg | 2603549 |
| Porphyrin 2 Reagent Powder Pillow, 10 mL | 2 | 100/pkg | 2603649 |

### Recommended standards

| Description | Unit | Item no. |
|---|---|---|
| Copper Standard Solution, 4 mg/L, 2-mL Pour-Rite Ampules | 20/pkg | 2605720 |
| Copper Standard Solution, 10-mg/L Cu | 100 mL | 12932 |
| Water, deionized | 4 L | 27256 |

## Optional reagents and apparatus

| Description | Unit | Item no. |
|---|---|---|
| Sodium Hydroxide Standard Solution, 5.0 N | 100 mL MDB | 245032 |
| Pipet, TenSette®, 0.1–1.0 mL | each | 1970001 |
| Pipet tips for TenSette® Pipet, 0.1–1.0 mL | 50/pkg | 2185696 |
| Flask, volumetric, Class A, 1000 mL glass | each | 1457453 |
| Sample cells, 1" square matched set | 8/pkg | 2495408 |
| Paper, pH, 0–14 pH range | 100/pkg | 2601300 |

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