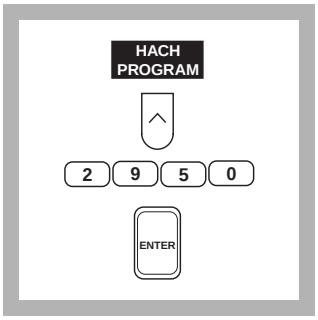
PHOSPHONATES

Method 8007 **Persulfate UV Oxidation Method***

Powder Pillows **(0-2.50 to 0-125 mg/L)**

Scope and Application: *For boiler and cooling water, water, wastewater and seawater.*
The estimated detection limit for program number 2950 depends on the sample volume. See Method Performance.

* Adapted from Blystone, P., Larson, P., *A Rapid Method for Analysis of Phosphonate Compounds*, International Water Conference, Pittsburgh, PA. (Oct 26–28, 1981)



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

Select the stored program number for phosphonates by pressing **2950** with the numeric keys.

Press: **ENTER**

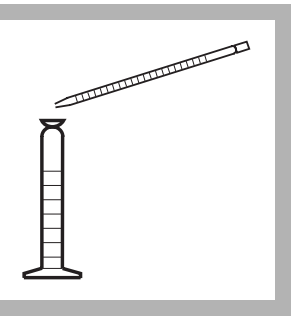
Note: *If samples cannot be analyzed immediately, see Sample Collection, Storage and Preservation following these steps.*

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

2. The display will show:

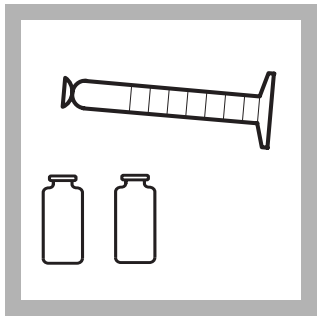
HACH PROGRAM: 2950
Phosphonates

The wavelength (λ), **890 nm**, is automatically selected.



3. Choose the appropriate sample size from *Table 1* below. Pipet the chosen volume into a 50-mL mixing graduated cylinder. If necessary, dilute the sample to 50 mL with deionized water and mix well.

Note: *Clean glassware with 1:1 hydrochloric acid, followed by a distilled water rinse. Do not use a commercial detergent.*



4. Fill a 1-inch sample cell to the 10-mL mark with diluted sample from Step 3 (this is the blank). Fill a second, 1-inch sample cell to the 25-mL mark with diluted sample from Step 3.

Table 1

Expected range (mg/L phosphonate)	Sample Volume (mL)
0–2.5	50
0–5	25
0–12.5	10
0–25	5
0–125	1

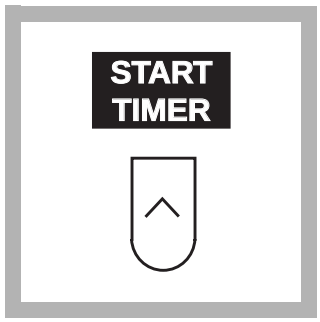
5. Add the contents of one Potassium Persulfate for Phosphonate Powder Pillow to the cell containing 25 mL of sample. Swirl to mix.

6. Insert the ultraviolet (UV) lamp into the sample cell.

Note: *Wear UV safety goggles while the lamp is on.*

Note: *Do not handle the lamp surface. Fingerprints will etch the glass. Wipe lamp with a soft, clean tissue between samples. Do not use phosphate detergents to wash glassware.*

Note: *A specially designed cord adapter (Cat. No. 19485-00) is available so two digestions can be performed at once using one power supply. A second UV lamp is required.*



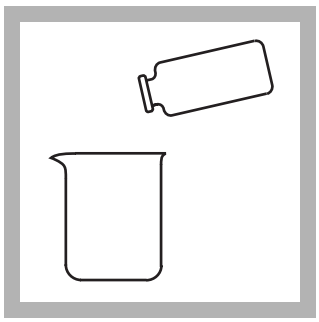
7. Turn the UV lamp on. Press the soft key under ***START TIMER***.

A 10-minute reaction period will begin.

Note: *Phosphonates are converted to orthophosphate in this step.*

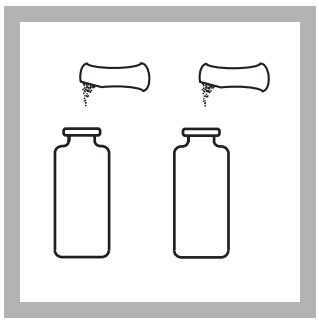
Note: *The digestion step is normally completed in less than 10 minutes. Contaminated samples or a weak lamp, however, can cause incomplete conversion to phosphate. Check conversion efficiency by running a longer digestion and seeing if readings increase.*

8. When the timer beeps, turn the UV lamp off and remove it from the sample.



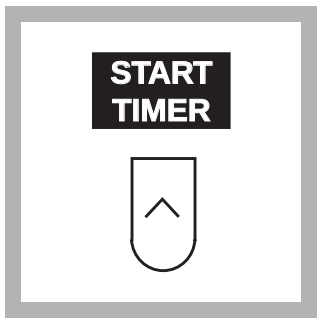
9. Pour off about 15 mL of sample into a 50-mL beaker so that 10 mL remains in the 1-inch sample cell. This is the prepared sample.

Note: *Use a beaker, rather than a sink or waste container, in case too much sample is poured out initially.*



10. Add the contents of one PhosVer 3 Phosphate Reagent Powder Pillow to the blank and prepared sample. Swirl immediately to mix.

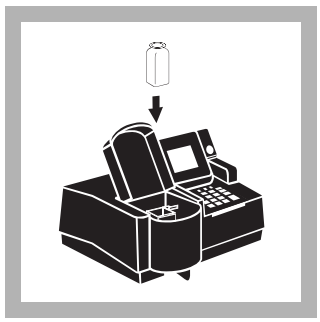
Note: *A blue color will develop if phosphate is present. Both sample and blank cells may develop color; the increase in sample color is proportional to the phosphonate concentration.*



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

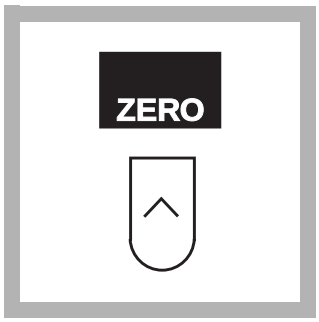
A 2-minute reaction period will begin.

Note: *If sample is colder than 15 °C, four minutes are required for color development.*



12. When the timer beeps, place the blank (undigested sample) into the cell holder. Close the light shield.

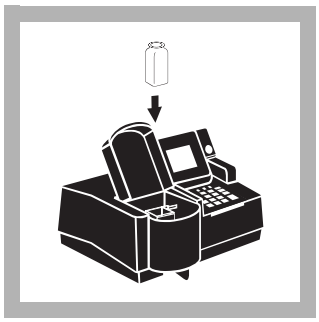
Note: *Do steps 13 and 14 within three minutes after the timer beeps.*



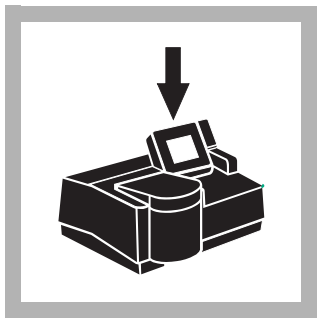
13. Press the soft key under ***ZERO***.

The display will show:

0.00 mg/L PO_4^{3-}



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



15. Read the mg/L phosphate from the display. Multiply this value by the appropriate multiplier in *Table 2* to obtain the actual concentration of phosphates in the sample.

See Table 3

16. Results can be expressed as active phosphonate by using the appropriate conversion factor from *Table 3*.

Active phosphonate (mg/L) = Phosphate concentration (Step 15) x Conversion Factor

Table 2

Sample volume	Multiplier
50	0.1
25	0.2
10	0.5
5	1.0
1	5.0
phosphonate concentration = instrument reading x multiplier	

Table 3

Phosphonate type	Conversion factor
PBTC	2.84
NTP	1.050
HEDPA	1.085
EDTMPA	1.148
HMDTMPA	1.295
DETPMPA	1.207
HPA	1.49
The result from Step 16 is the active phosphonate. To determine the concentration of the product being used (e.g., NTP), divide the active phosphonate value by the percent active phosphonate value on the product label.	

Interferences

When testing a 5-mL sample volume, the following may interfere if present in concentrations exceeding those listed below:

Table 4 Interfering Substances and Suggested Treatments

Interfering Substance	Interference Levels and Treatments
Aluminum	100 mg/L
Arsenate	Interferes at all levels
Benzotriazole	10 mg/L
Bicarbonate	1000 mg/L
Bromide	100 mg/L
Calcium	5000 mg/L
CDTA	100 mg/L
Chloride	5000 mg/L

Table 4 Interfering Substances and Suggested Treatments (Continued)

Interfering Substance	Interference Levels and Treatments
Chromate	100 mg/L
Copper	100 mg/L
Cyanide	100 mg/L. Increase the UV digestion to 30 minutes.
Diethanoldithiocarbamate	50 mg/L
EDTA	100 mg/L
Iron	200 mg/L
Nitrate	200 mg/L
NTA	250 mg/L
Orthophosphate	15 mg/L
Phosphites and organophosphorus compounds	React quantitatively. Meta- and polyphosphates do not interfere.
Silica	500 mg/L
Silicate	100 mg/L
Sulfate	2000 mg/L
Sulfide	Interferes at all levels
Sulfite	100 mg/L
Thiourea	10 mg/L
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment.

The interference levels will decrease as the sample size increases. For example, copper does not interfere at or below 100 mg/L for a 5.00 mL sample. If the sample volume is increased to 10 mL, copper will begin to interfere above 50 mg/L.

Sample Collection, Storage and Preservation

Collect samples in acid-cleaned (1:1 HCl) plastic or glass bottles that have been rinsed with distilled water. Do not use a commercial detergent. If prompt analysis is impossible, preserve the sample by adjusting to pH 2 or less with sulfuric acid (about 2 mL per liter). Store at 4 °C (39 °F). Preserved samples may be stored at least 24 hours. Correct the test result for volume additions; see Section *1.2.2 Correcting for Volume Additions*.

Accuracy Check

Ideally, a solution containing the phosphonate product being used should be prepared. This will check the UV conversion of phosphonate to orthophosphate. Or, a phosphate standard can be used to check the accuracy or the colorimetric part of the method.

Standard Solution

A 1-mg/L Phosphate Standard Solution (available from Hach) can be used to check accuracy. Use 10 mL of this standard in place of the prepared sample in Step 9. Use deionized water for the blank. A multiplier value from *Table 2* is not needed. The result should be 10.0 mg/L phosphate, due to a factor of 10 in calibration.

Method Performance

Precision
Standard: 1.00 mg/L PO_4^{3-}

Program	95% Confidence Limits
2950	0.98–1.02 mg/L PO_4^{3-}

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

Estimated Detection Limit
The EDL depends on the sample volume.

Range (mg/L)	Volume (mL)	EDL (mg/L)
0–2.5	50	0.045
0–5	25	0.09
0–12.5	10	0.23
0–25	5	0.45
0–125	1	2.25

EDL is expressed as PO_4^{3-} in this table. Use *Table 3* to express as a specific phosphonate.

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: 2950

Portion of Curve	ΔAbs	ΔConcentration
0.010 Abs	0.010	0.16813 mg/L
12.5 mg/L	0.010	0.177409 mg/L
22.5 mg/L	0.010	0.184591 mg/L

Sensitivity is expressed as PO_4^{3-} in this table. Use *Table 3* to convert to a specific phosphonate.

See Section *1.5.3 Sensitivity Explained* for more information.

Calibration Standard Preparation

To perform a phosphonate calibration using the Persulfate UV Oxidation method, phosphate standard solutions are substituted for digested phosphonate samples in Step 9 of the procedure. Use a 10-mg/L Phosphate Standard Solution (Cat. No 14204-16). Prepare calibration standards containing 0.300, 1.500 and 2.400 mg/L phosphate as follows:

a. Into three different 100-mL Class A volumetric flasks, pipet 3.00, 15.00 and 24.00 mL of the 10-mg/L Phosphate Standard Solution using Class A glassware.

b. Dilute to the mark with deionized water. Mix thoroughly.

Because of the factor of 10 built into the procedure (*i.e.* the multiplier for an undiluted sample in Step 3 is 0.1), the 0.3, 1.5 and 2.4 mg/L standards should be entered as 3.0, 15.0, and 24.0 mg/L PO_4^{3-}.

Using the above standards in place of the sample in Step 9 and deionized water as the blank, generate a calibration curve following the calibration procedure described in the *User-Entered Programs* section of the *DR/4000 Spectrophotometer Instrument Manual*.

Summary of Method

This method is directly applicable to boiler and cooling tower samples. The procedure is based on a UV catalyzed oxidation of phosphonate to orthophosphate. The orthophosphate reacts with the molybdate in the PhosVer 3 reagent to form a phosphomolybdate complex. This complex is reduced by the ascorbic acid in the PhosVer 3, yielding a blue color which is proportional to the phosphonate present in the original 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 *3*.

Pollution Prevention and Waste Management

For information on pollution prevention and waste management, refer to Section *3*.

REQUIRED REAGENTS AND STANDARDS

	Cat. No
Phosphonate Reagent Set for 10 mL sample (100 tests)	24297-00
Includes: (1) 21060-69, (1) 20847-69, (1) 171-02	

Description	Quantity Required Per Test	Unit	Cat. No.
PhosVer 3 Phosphate Reagent Powder Pillows, 10-mL	2 pillows	100/pkg	21060-69
Potassium Persulfate Powder Pillow for Phosphonate	1 pillow	100/pkg	20847-69
Water, deionized	varies	4 liters	272-56

REQUIRED EQUIPMENT AND SUPPLIES

Beaker, 50-mL	1	each	500-41
Cylinder, mixing, graduated, 50-mL	1	each	1896-41
DR/4000 1-Inch Cell Adapter	1	each	48190-00
Goggles, UV safety	1	each	21134-00
Pipet, serological, 10-mL	1	each	532-38
Safety bulb	1	each	14651-00
UV Lamp with power supply, 115 VAC	1	each	20828-00
or			
UV Lamp with power supply, 230 VAC	1	each	20828-02

OPTIONAL REAGENTS AND STANDARDS

Hydrochloric Acid Standard Solution, 6.0 N (1:1)	500 mL	884-49
Sulfuric Acid, ACS, concentrated	500 mL	979-49
Phosphate Standard Solution, 10-mg/L	946 mL	14204-16

OPTIONAL EQUIPMENT AND SUPPLIES

Cord Adapter, single to dual UV lamp	each	19485-00
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
pH Paper, pH 1.0 to 11.0	5 rolls/pkg	391-33
Pipet, serological, 2-mL	each	532-36
Pipet, volumetric, Class A, 3.00-mL	each	14515-03
Pipet, volumetric, Class A, 9.00-mL	each	14515-09
Pipet, volumetric, Class A, 15.00-mL	each	14515-39
Pipet Filler, safety bulb	each	14651-00
UV Lamp without power supply	each	20823-00

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