



✓ Method 8013

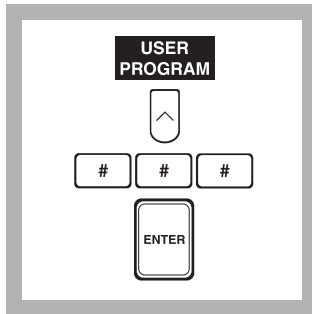
Silver Diethyldithiocarbamate Method*

(0 to 0.200 mg/L)

Scope and Application: For water, wastewater and seawater; distillation is required; USEPA accepted for reporting for drinking and wastewater analysis (digestion required).** See Section 2 for digestion procedure.

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

** Procedure is equivalent to USEPA method 206.4 for wastewater and Standard Method 3500-As for drinking water analyses.



1. This procedure requires a user-entered calibration for each new lot of arsenic absorber solution. See *Calibration Standard Preparation* section. Press the soft key under **USER PROGRAM**. Select the stored program for arsenic (As) using the numeric keys.

Press: **ENTER**

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

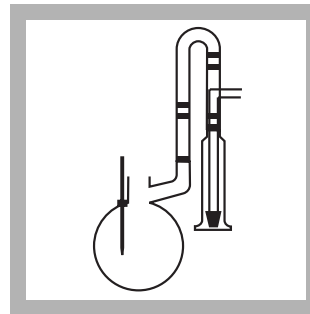
Note: The Flow Cell and Sipper Modules cannot be used with this procedure.



2. The display will show:
**HACH PROGRAM: ###
Arsenic As**

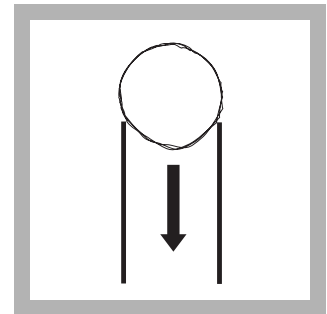
The wavelength (λ), **520 nm**, is automatically selected.

Note: ### refers to the number assigned during calibration.

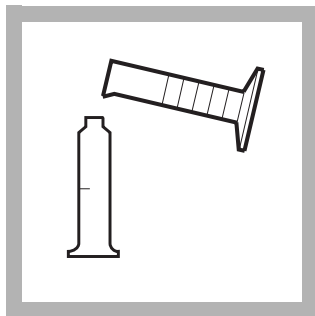


3. Prepare the Hach Distillation Apparatus for arsenic recovery. Place it under a fume hood to vent toxic fumes.

Note: See the Hach Distillation Manual for assembly instructions.

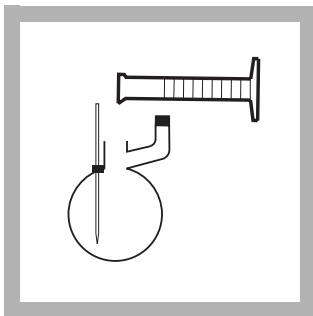


4. Dampen a cotton ball with 10% Lead Acetate Solution. Place it in the gas scrubber. Be certain the cotton seals against the glass.

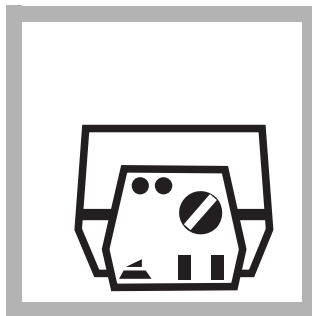


5. Measure 25 mL of prepared arsenic absorber solution into the cylinder/gas bubbler assembly with a graduated cylinder. Attach it to the distillation apparatus.

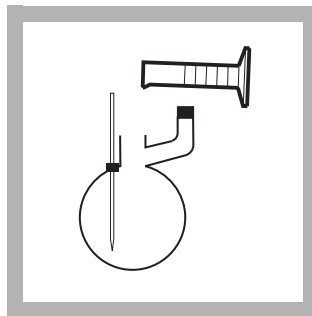
Note: Prepare the arsenic absorber solution as directed under Reagent Preparation below.



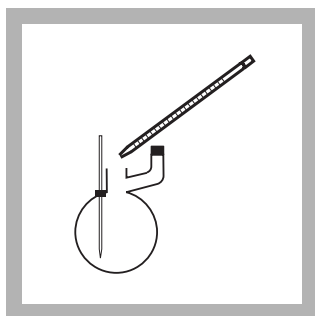
6. Measure 250 mL of sample into the distillation flask using a graduated cylinder.



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

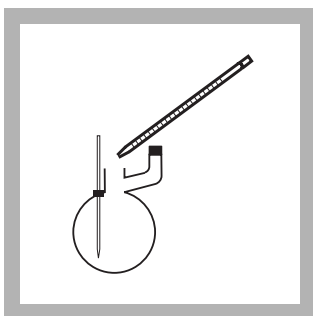


8. Add 25 mL of Hydrochloric Acid, ACS, to the distillation flask using a graduated cylinder.



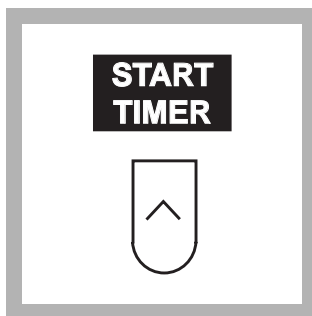
9. Add 1 mL of Stannous Chloride Solution to the flask.

Note: Use a serological pipet to measure the solution.

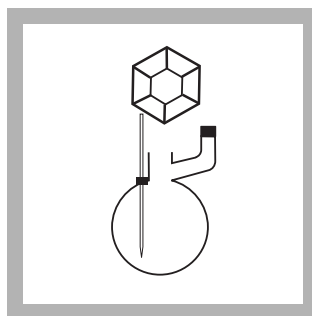


10. Add 3 mL of Potassium Iodide Solution to the flask. Cap.

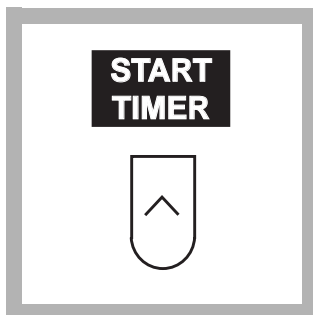
Note: Use a serological pipet to measure the solution.



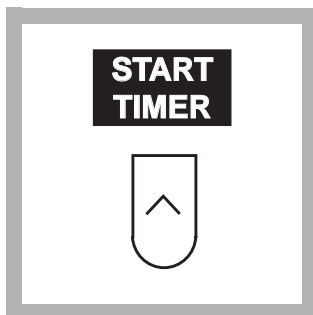
11. Press the soft key under **START TIMER**. A 15-minute reaction period will begin.



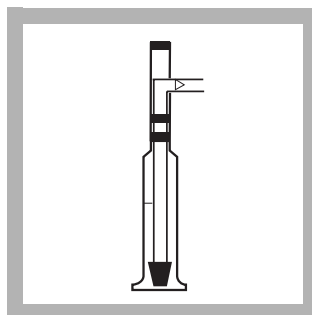
12. When the timer beeps, add 6.0 g of 20-mesh zinc to the flask. Cap immediately.



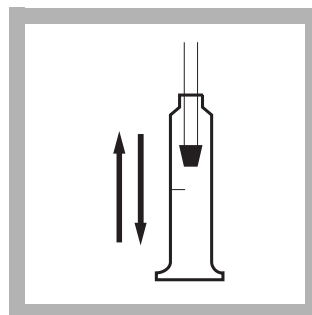
13. Set the heat control to 3.
Press the soft key under **START TIMER**.
A second 15-minute reaction period will begin.



14. When the timer beeps, set the heat control to 1.
Press the soft key under **START TIMER**.
A third 15-minute reaction period will begin.



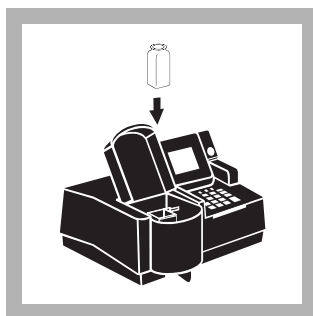
15. When the timer beeps, turn off the heater. Remove the cylinder/gas bubbler assembly as a unit.



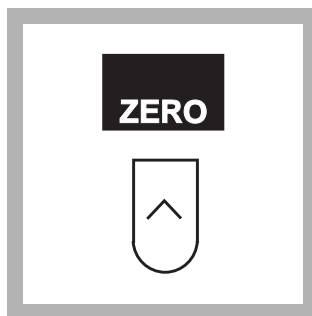
16. Rinse the gas bubbler by moving it up and down in the arsenic absorber solution.



17. Fill a dry sample cell with unreacted arsenic absorber solution (the blank). Stopper. Place it into the cell holder.



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

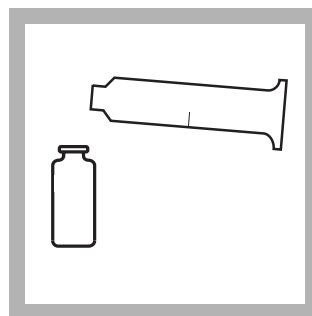


19. Press the soft key under **ZERO**.

The display will show:

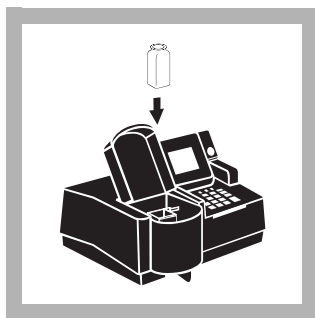
0.000 mg/L As

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. Some units may not be applicable for this calibration even though they appear as options.



20. Pour the reacted arsenic absorber sample into a sample cell. Stopper.

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



21. Place the reacted sample into the cell holder. Close the light shield. Results in mg/L arsenic (or chosen units) will be displayed.

Note: See *Pollution Prevention and Waste Management* following these steps about proper disposal of arsenic solutions.

Interferences

Table 1 Interfering Substances and Suggested Treatments

Interfering Substance	Interference Levels and Treatments
Antimony Salts	May interfere with color development

Sample Collection, Storage and Preservation

Collect samples in acid washed glass or plastic bottles. Adjust the pH to 2 or less with sulfuric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature. Correct the test result for volume additions; see Section 1.2.2 *Correcting for Volume Additions*.

Reagent Preparation

Prepare the arsenic absorber solution as follows:

1. Weigh 1.00 g of silver diethyldithiocarbamate on an analytical balance.
2. Transfer the powder to a 200-mL volumetric flask. Dilute to volume with pyridine. You must use pyridine only in a fume hood and wear chemical resistant gloves. Read the MSDS before using pyridine.
3. Mix well to dissolve. Store the reagent, tightly sealed, in an amber bottle. The reagent is stable for one month if stored in this manner. Larger volumes of reagent can be prepared if the reagent is used within one month.

Accuracy Check

Standard Additions Method

- a. Leave the unspiked sample in the sample compartment. Verify that the units displayed are in mg/L. Select standard additions mode by pressing the soft keys under **OPTIONS, (MORE)** and then **STD ADD**.
- b. Press **ENTER** to accept the default sample volume (mL), 250.
- c. Press **ENTER** to accept the default standard concentration (mg/L), 100.
- d. Press the soft key under **ENTRY DONE**.
- e. Prepare a 100-mg/L arsenic working standard by pipetting 10.0 mL of Arsenic Standard Solution, 1000-mg/L As (Cat. No. 14571-42) into a 100-mL volumetric flask. Dilute to volume with deionized water.
- f. Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively to three 250-mL samples and mix each thoroughly.
- g. Analyze each standard addition sample as described above. Accept the standard additions reading by pressing the soft key under **READ** each time. Each addition 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 Solution Method

To check accuracy, use a 0.100-mg/L arsenic standard solution prepared as follows:

- a. Pipet 1 mL of a 1000-mg/L Arsenic Standard Solution into a 100-mL Class A volumetric flask. Dilute to the mark with deionized water and mix thoroughly.
- b. Pipet 1 mL of the solution prepared in step a into a 100-mL class A volumetric flask. Dilute to the mark with deionized water and mix thoroughly. This is a 0.100-mg/L arsenic standard solution.

Calibration Standard Preparation

Standard Preparation

Perform a new calibration for each lot of arsenic absorber solution. Prepare a 10.0-mg/L arsenic working standard by pipetting 10.0 mL of Arsenic Standard Solution, 1000-mg/L As into a 1000-mL volumetric flask. Dilute to volume with deionized water.

Into three different 500-mL volumetric flasks, pipet 1.0, 2.0, and 10.0 mL of the 10.0-mg/L As stock solution using Class A glassware. Dilute to the mark with deionized water and mix thoroughly. These standards have concentrations of 0.02, 0.04, and 0.20 mg/L As.

User Programming

- a. Start from the “MAIN MENU.” Press the soft key under **USER PROGRAM**.

- b. If you have not performed an arsenic calibration before, press the soft key under **CREATE**. Key any available program number you wish to use for arsenic testing. Press **ENTER**. Press the soft key under **COPY PROGRAM**. Select program number **1050** and press **ENTER**. If you already have a working arsenic program, press the soft key under **EDIT**, select the program number and press **ENTER**.
- c. Press the **DOWN ARROW** key until you highlight the parameter **Calib. table**. Press the soft key under **EDIT TABLE**. Press the **UP ARROW** key to highlight the very first concentration in the list. Press the soft key under **EDIT ABS**. Press **CE** and then **ENTER** to erase the first, inaccurate, absorbance value. Repeat to erase all the absorbance values. Press the soft key under **ENTRY DONE**.

Note: A user calibration **MUST** be performed to obtain accurate results. The original absorbance values are generic and are included only as an example.

- d. Note which mg/L value is highlighted. Perform steps 3 through 21 of the arsenic Silver Diethyldithiocarbamate Method on deionized water (this is the reagent blank). Place the sample cell into the cell holder. Press the soft key under **ZERO**. Then press the soft key under **READ**. Repeat steps 3 through 21 of the procedure on the other arsenic standards. Place the prepared samples in the cell holder and press the soft key under **READ** to accept the absorbance value.
- e. In the **Curve fit:** display, press the soft key under **NEXT FORMULA** until **C = a + bA** is displayed. Press the soft key under **FORCE 0:** once so that **ON** is selected. Press **EXIT** until **Store Changes?** is displayed. Press the soft key under **YES**. The program is ready for use.

Note: Some variations of the calibration procedure are possible. See the DR/4000 Instrument Manual for details.

Summary of Method

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

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

The arsenic absorber in this test is a silver solution in pyridine. Both silver (D011) and pyridine (D038) are regulated by the Federal RCRA as hazardous waste. In addition, the cotton ball soaked in lead acetate (D008) solution is a hazardous waste. These materials should not be poured down the drain. See Section 3 for more information on proper disposal of these materials.

REQUIRED REAGENTS AND STANDARDS

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

REQUIRED EQUIPMENT AND SUPPLIES

Balance, analytical, 110/220 VAC.....	1	each.....	26103-00
Balls, cotton.....	1	100/pkg.....	2572-01
Boat, weighing	2	500/pkg.....	21790-00
Bottle, amber, 237-mL, glass	1	6/pkg.....	7144-41
Cap, polypropylene, for amber bottle.....	1	6/pkg.....	21667-06
Cylinder, graduated, 25-mL	2	each.....	508-40
Cylinder, graduated, 250-mL	1	each.....	508-46
Distillation Apparatus, Arsenic Accessories.....	1	set.....	22654-00
Distillation Apparatus, General Purpose Accessories.....	1	set.....	22653-00
DR/4000 1-Inch Cell Adapter	1	each.....	48190-00
Flask, volumetric, 1000-mL, Class A, with glass stopper.....	1	each.....	14574-53
Flask, volumetric, 200-mL, Class A	1	each.....	14574-45
Flask, volumetric, 500-mL, Class A	6	each.....	14574-49
Pipet Filler, safety bulb.....	1	each.....	14651-00
Pipet, serological, 5-mL	2	each.....	532-37
Pipet, volumetric, Class A, 1.00-mL.....	2	each.....	14515-35
Pipet, volumetric, Class A, 2.00-mL.....	1	each.....	14515-36
Pipet, volumetric, Class A, 4.00-mL.....	1	each.....	14515-04
Pipet, volumetric, Class A, 6.00-mL.....	1	each.....	14515-06
Pipet, volumetric, Class A, 8.00-mL.....	1	each.....	14515-08
Pipet, volumetric, Class A, 10.00-mL.....	1	each.....	14515-38
Stopper, hollow, poly., No. 1	2	6/pkg.....	14480-00
Select one based on available voltage:			
Distillation Apparatus Heater, 115 VAC, 60 Hz		each.....	22744-00
Distillation Apparatus Heater, 230 VAC, 50 Hz		each.....	22744-02

OPTIONAL REAGENTS AND STANDARDS

Description	Unit	Cat. No.
Hydrochloric Acid, ACS	2.5 liters.....	134-06
Nitric Acid, ACS	500 mL.....	152-49
Nitric Acid Solution, 1:1	500 mL.....	2540-49
Pyridine, ACS.....	4 liters.....	14469-17
Water, deionized.....	4 liters.....	272-56

ARSENIC, continued

OPTIONAL EQUIPMENT AND SUPPLIES

Description	Quantity Required per test	Unit	Cat. No.
DR/4000 Carousel Module Kit		each.....	48090-02
Flask, volumetric, Class A, 100-mL		each.....	14574-42
Gloves, chemical resistant:			
Size 7-7½.....		pair.....	24101-02
Size 8-8½.....		pair.....	24101-03
Size 9-9½.....		pair.....	24101-04
Size 10.....		pair.....	24101-05
Size 11.....		pair.....	24101-06
pH Meter, <i>sensio</i> TM 1, portable.....		each.....	51700-00
pH Indicator Paper, 1.0 to 11.0 pH.....	5 rolls/pkg		391-33
Pipet, serological, 2-mL		each.....	532-36
Pipet, TenSette, 0.1 to 1.0 mL.....		each.....	19700-01
Pipet Tips, for TenSette Pipet 19700-01	50/pkg		21856-96



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