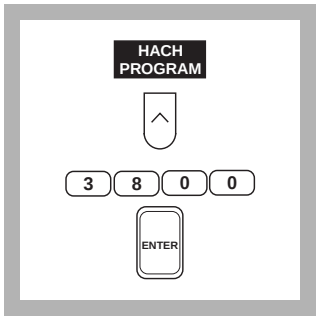
VOLATILE ACIDS

Method 8196 **Esterification Method***

(0 to 2800 mg/L)

Scope and Application: *For digestor sludges.*
The estimated detection limit for program number 3800 is 12 mg/L as acetic acid (HOAC).

* Adapted from *The Analyst*, 87, 949 (1962)

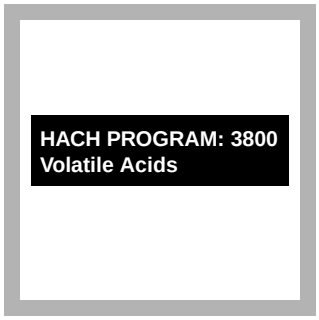


1. Press the soft key under ***HACH PROGRAM***.

Select the stored program number for volatile acids by pressing **3 8 0 0** with the numeric keys.

Press: **ENTER**

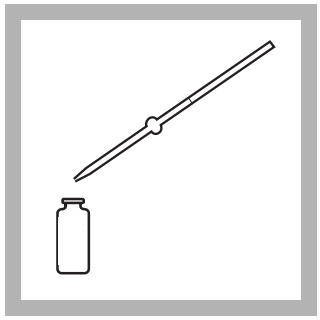
Note: *If samples cannot be analyzed immediately, see Sample Collection, Preservation and Storage following these steps.*



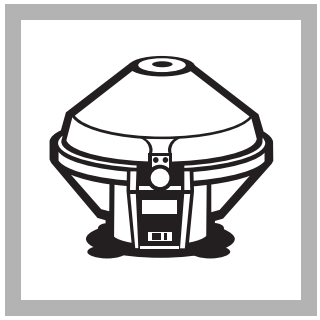
2. The display will show:

HACH PROGRAM: 3800
Volatile Acids

The wavelength (λ), **495 nm**, is automatically selected.

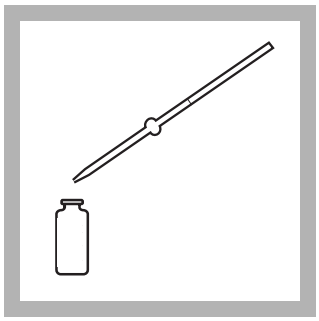


3. Pipet 0.5 mL of deionized water into a dry 25-mL sample cell (the blank).



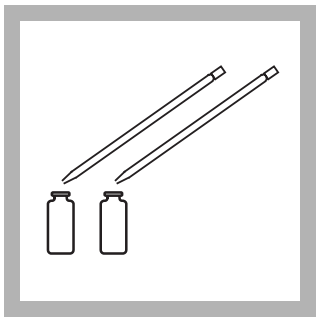
4. Filter or centrifuge 25 mL of sample using the labware listed under *REQUIRED EQUIPMENT AND SUPPLIES*.

Note: *Centrifuging is faster than filtration.*

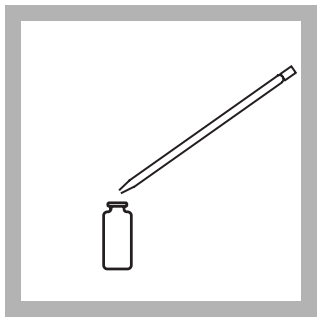


5. Pipet 0.5 mL of the filtrate or supernatant into another dry 25-mL sample cell (the prepared sample).

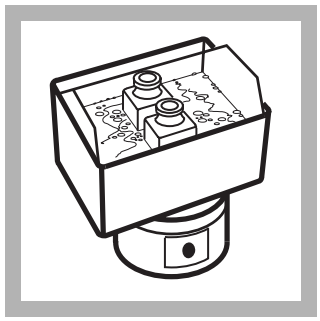
Note: *For proof of accuracy, use 0.5 mL of a 500-mg/L volatile acid standard solution in place of the sample (see Accuracy Check).*



6. Pipet 1.5 mL of ethylene glycol into each sample cell. Swirl to mix.

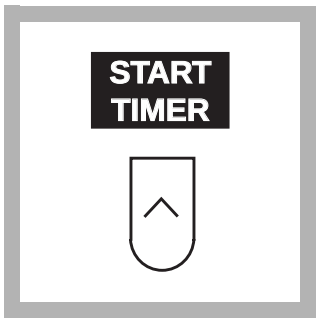


7. Pipet 0.2 mL of 19.2 N Sulfuric Acid Standard Solution into each cell. Swirl to mix.



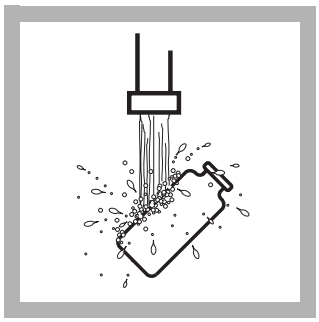
8. Place both cells into a boiling water bath.

Note: *You may boil the sample cells in a 600-mL beaker.*

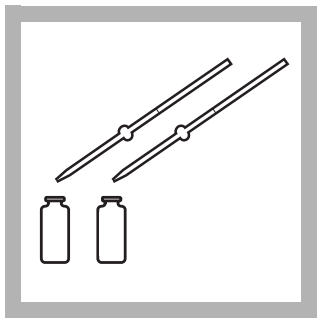


9. Press the soft key under ***START TIMER.***

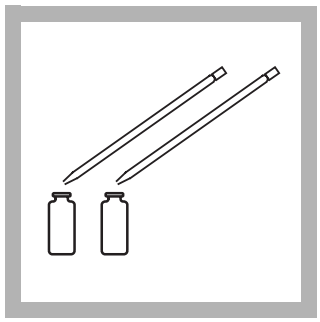
Note: *A 3-minute reaction period will begin.*



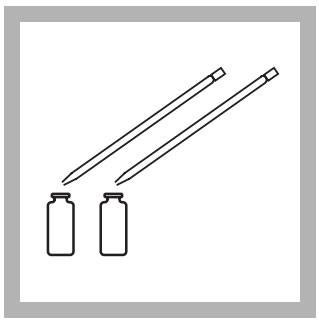
10. When the timer beeps, cool the solutions to 25 °C (until the cell feels cold) with running tap water.



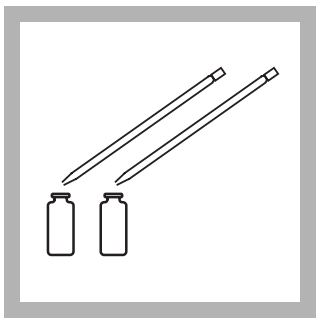
11. Using a pipet filler, pipet 0.5 mL of Hydroxylamine Hydrochloride Solution into each cell. Swirl to mix.



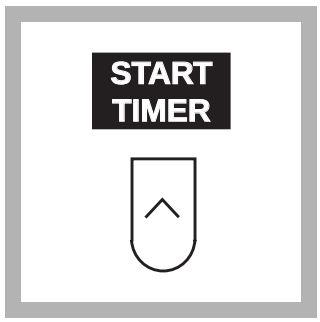
12. Using a pipet filler, pipet 2.0 mL of 4.5 N Sodium Hydroxide Standard Solution into each cell. Swirl to mix.



13. Add 10 mL of Ferric Chloride Sulfuric Acid Solution to each cell. Swirl to mix.



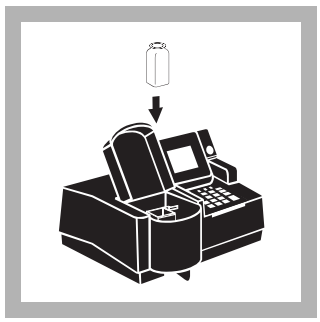
14. Add 10 mL of deionized water into each cell. Swirl to mix.



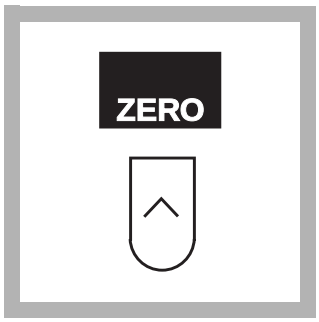
15. Immediately press the soft key under ***START TIMER.***

Another 3-minute reaction period will begin.

Note: *During this 3-minute reaction period, complete Steps 16-17.*



16. Blot each sample cell dry. Immediately place the blank in the cell holder. Close the light shield.

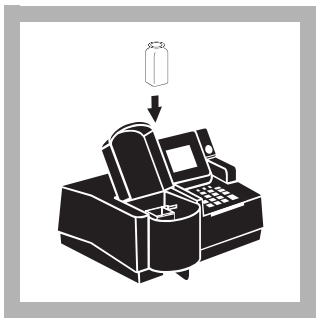


17. Press the soft key under ***ZERO***.

The display will show:

0 mg/L HOAC

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.*



18. When the timer beeps, immediately place the prepared sample in the cell holder. Close the light shield. Results in mg/L volatile acids as acetic acid will be displayed.

Sample Collection, Preservation and Storage

Collect samples in clean plastic or glass bottles. Analyze as soon as possible after collection. Samples can be stored for up to 24 hours by cooling to 4 °C (39 °F) or below. Warm samples to room temperature before analysis.

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), 25.

c. Press **ENTER** to accept the default standard concentration (mg/L), 62,500.

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

e. Snap the neck off a Volatile Acid Voluette® Ampule Standard, 62,500 mg/L as acetic acid.

f. Use the TenSette® Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to three 25-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
Prepare a 500-mg/L volatile acid standard solution by pipetting 4.00 mL of a 62,500-mg/L Volatile Acid Standard Solution into a 500-mL Class A volumetric flask. Dilute to volume with deionized water. Prepare this solution daily. Perform the esterification procedure as described above.

To adjust the calibration curve using the reading obtained with the 500-mg/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 500 mg/L as acetic acid (HOAC)

Program	95% Confidence Limits
3800	492–507 mg/L HOAC

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

Estimated Detection Limit

Program	EDL
3800	12 mg/L as HOAC

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 40 CFR part 136, appendix B, see Section *1.5.1*.

Sensitivity
Program Number: 3800

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	23.4 mg/L

See Section *1.5.3 Sensitivity Explained* for more information.

Calibration Standard Preparation

To perform a volatile acids calibration using the esterification method, use the 62,500-mg/L Volatile Acids Standard Solution (Cat. No. 14270-10) listed under optional reagents and standards. Prepare standards containing 313, 625, 938, 1250, 1563, 2188, and 2500 mg/L volatile acids as follows:

a. Pipet 1.00, 2.00, 3.00, 4.00, 5.00, 7.00, and 8.00 mL of the 62,500-mg/L Volatile Acids Standard Solution into seven different 200-mL Class A volumetric flasks, using Class A glassware.

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

c. Using the esterification 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 volatile acid test is designed specifically for determining volatile acids in digestor sludges. The method is based on esterification of the carboxylic acids present in the sample and subsequent determination of the esters by the ferric hydroxamate reaction. All volatile acids present are reported as their equivalent mg/L as acetic acid.

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.
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	Unit	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 MDB	2038-32
Water, deionized	20.5 mL	4 L	272-56

REQUIRED EQUIPMENT AND SUPPLIES

Cylinder, graduated, 10-mL	1	each	508-38
DR/4000 1-Inch Cell Adapter	1	each	48190-00
Filter Paper, folded, 12.5-cm	1	100/pkg	1894-57
Finger Cots	2	2/pkg	14647-02
Flask, Erlenmeyer, 50-mL	1	each	505-41

REQUIRED EQUIPMENT AND SUPPLIES((continued)

Funnel, poly, 65-mm	1	each	1083-67
Hot Plate, 4" micro, 120 VAC	1	each	12067-01
Hot Plate, 4" micro, 240 VAC	1	each	12067-02
Pipet, Filler, safety bulb	1	each	14651-00
Pipet, TenSette®, 1.0- to 10.0-mL	1	each	19700-10
Pipet Tips, for 19700-10 Pipet	2	50/pkg	21997-96
Pipet, serological, 2-mL	1	each	532-36
Pipet, volumetric, Class A, 0.50-mL	1	each	14515-34
Pipet, volumetric, Class A, 10.00-mL	1	each	14515-38
Water Bath and Rack	1	each	1955-55

OPTIONAL REAGENTS AND STANDARDS

Description	Unit	Cat. No.
Volatile Acids Standard Solution, 10-mL Voluette® Ampule, 62,500 mg/L as HOAC	16/pkg	14270-10
Volatile Acids Standard Solution, 1000-mg/L as HOAC	100 mL	14205-42

OPTIONAL EQUIPMENT AND SUPPLIES

Ampule Breaker Kit		each	21968-00
Aspirator, Nalgene* vacuum pump		each	2131-00
Bottle, wash, 500-mL		each	620-11
Beaker, 600-mL		each	500-52
Centrifuge, Spinette, 115 VAC, 60 Hz		each	22413-00
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, 100-mL		each	508-42
Cylinder, graduated, 250-mL		each	508-46
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
Filter Paper, 9-cm dia.		100/pkg	506-55
Flask, filtering, 500-mL		each	546-49
Flask, volumetric, Class A, 200-mL		each	14574-45
Funnel, Buchner		each	550-87
Pipet, TenSette, 0.1- to 1.0-mL		each	19700-01
Pipet Tips, for 19700-01 Pipet		50/pkg	21856-96
Pipet, serological, 5-mL		each	532-37
Pipet, volumetric, Class A, 1.00-mL		each	14515-35
Pipet, volumetric, Class A, 2.00-mL		each	14515-36
Pipet, volumetric, Class A, 3.00-mL		each	14515-03
Pipet, volumetric, Class A, 4.00-mL		each	14515-04
Pipet, volumetric, Class A, 5.00-mL		each	14515-37
Pipet, volumetric, Class A, 7.00-mL		each	14515-07
Pipet, volumetric, Class A, 8.00-mL		each	14515-08
Test Tube Holder		each	634-00
Tubing, rubber		3.6 m (12 ft)	560-18
Tweezers, balance weight, plastic		each	14282-00

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