Volatile Acids

DOC316.53.01144

Esterification Method[1]

Method 8196

27 to 2800 mg/L (as acetic acid)

Reagent Solution

Scope and application: For digestor sludges.

[1] Adapted from The Analyst, 87, 949 (1962).

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
DR 6000 DR 3800 DR 2800 DR 2700 DR 1900	The fill line is to the right.	2495402 
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The orientation mark is toward the user.	2401906 

Before starting

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
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
Centrifuge	1
Centrifuge tubes and caps	2
Cylinder, 10-mL graduated	1
Ethylene Glycol	3 mL
Ferric Chloride-Sulfuric Acid Solution	20 mL

Items to collect (continued)

Description	Quantity
Funnel and filter paper	varies
Hot Plate	1
Hydroxylamine Hydrochloride Solution, 100-g/L	1 mL
Pipet filler	1
Pipet, 2-mL	1
Pipet, Class A volumetric, 0.50-mL[1]	1
Pipet, Class A volumetric, 10-mL	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2
Sodium Hydroxide Standard Solution, 4.5 N	4 mL
Sulfuric Acid Standard Solution, 19.2 N	0.4 mL
Water bath and rack	1
Water, deionized	20.5 mL

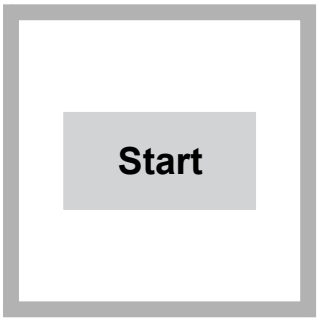
[1] A TenSette Pipet can be used in place of individual pipets in this procedure.

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

Sample collection and storage

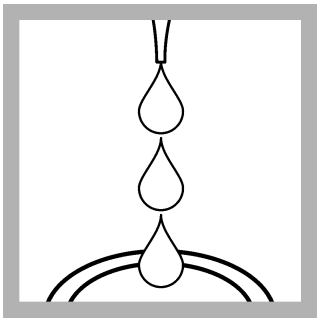
- Collect samples in clean glass or plastic bottles.
- To preserve samples for later analysis, keep the samples at or below 6 °C (43 °F) for up to 24 hours.
- Let the sample temperature increase to room temperature before analysis.

Esterification method

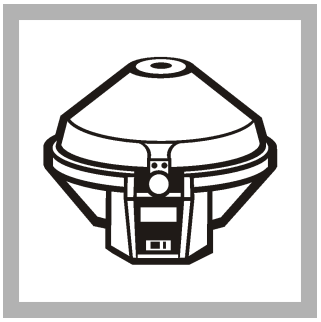


1. Start program **770 Volatile Acids**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

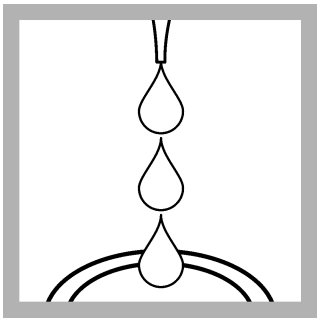
Note: *Although the program name can be different between instruments, the program number does not change.*



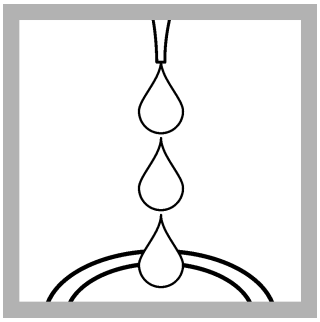
2. Prepare the blank: Use a pipet to add 0.5 mL of deionized water to a sample cell.



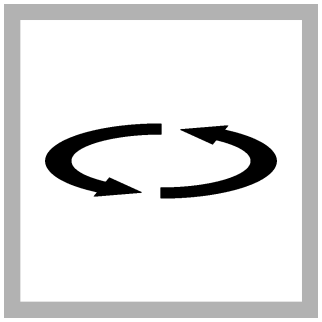
3. Use a filter or a centrifuge to separate 10 mL of sample.



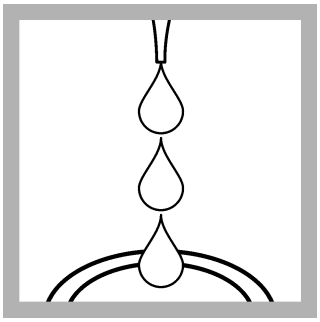
4. Prepare the sample: Use a pipet to add 0.5 mL of the filtrate or supernatant to a second sample cell.



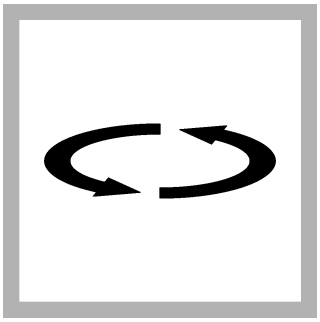
5. Add 1.5 mL of Ethylene Glycol to each sample cell.



6. Swirl to mix.



7. Add 0.2 mL of 19.2 N Sulfuric Acid to each sample cell.

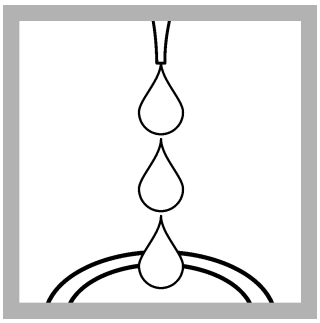


8. Swirl to mix.

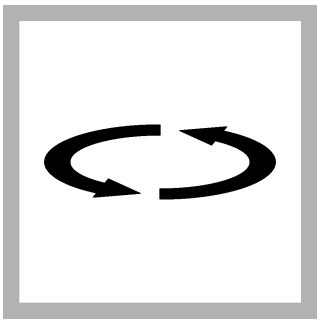
9. Put both cells into a boiling water bath.
The sample cells can also be boiled in a 500-mL beaker.

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

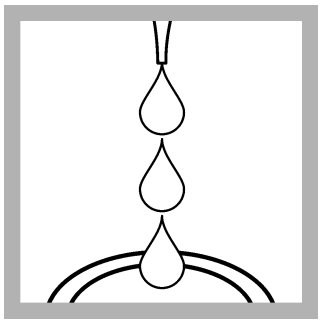
11. When the timer expires, use a cold water bath to cool the samples to 25 °C (the cells will feel cold).



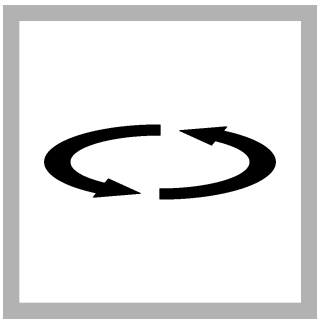
12. Add 0.5 mL of Hydroxylamine Hydrochloride Solution to each sample cell.



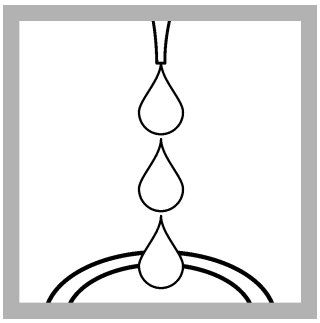
13. Swirl to mix.



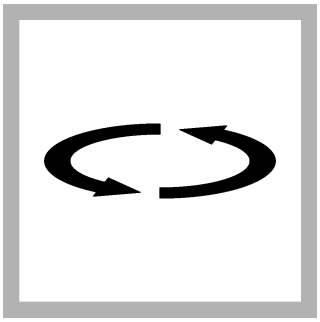
14. Add 2.0 mL of 4.5 N Sodium Hydroxide Standard Solution to each cell.



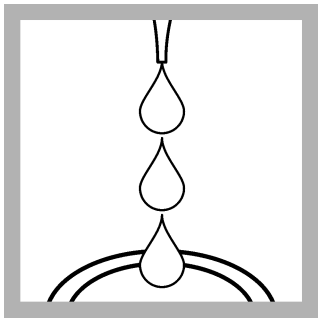
15. Swirl to mix.



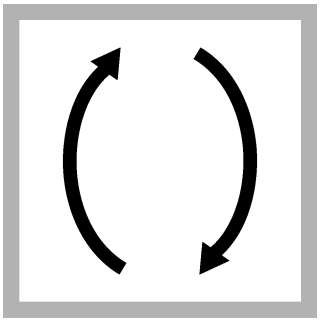
16. Add 10 mL of Ferric Chloride Sulfuric Acid Solution to each sample cell.



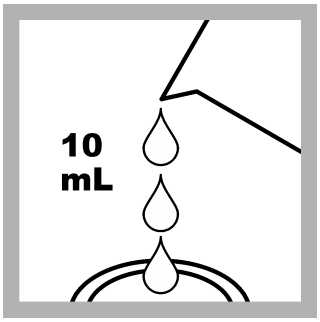
17. Swirl to mix.



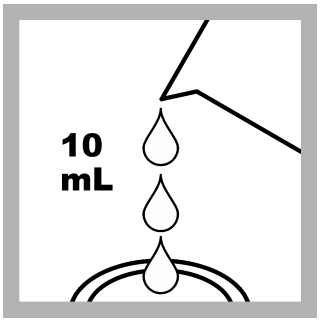
18. Add 10 mL of deionized water to each sample cell.



19. Put the stopper on both cells. Invert both cells to mix.



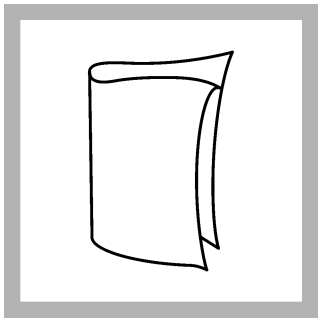
20. Transfer 10 mL of the blank solution to a clean sample cell.



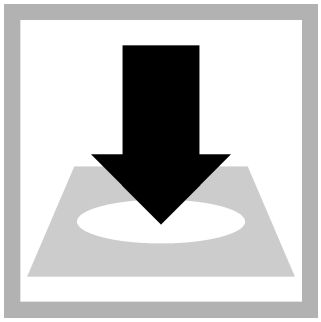
21. Transfer 10 mL of the prepared sample solution to a clean sample cell.

22. Start the instrument timer. A second 3-minute reaction time starts.

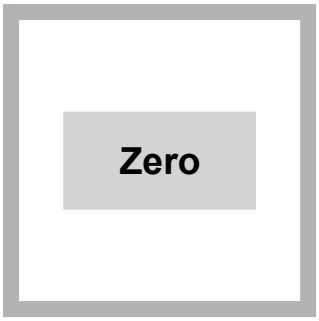
Set the instrument to zero during this reaction time.



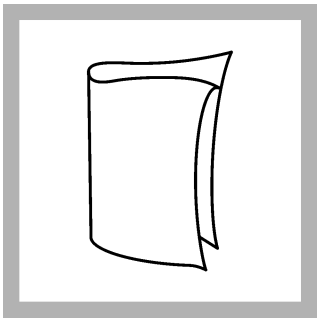
23. When the timer expires, clean the blank sample cell.



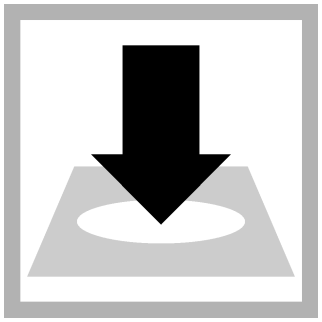
24. Insert the blank into the cell holder.



25. Push **ZERO**. The display shows 0 mg/L HOAC.



26. Clean the prepared sample cell.



27. Insert the prepared sample into the cell holder.

28. Push **READ**. Results show in mg/L HOAC.

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:

- Volatile Acid Voluette® Ampule Standard, 62,500-mg/L as acetic acid
- Ampule breaker
- Pipet, TenSette®, 0.1–1.0 mL and tips
- Mixing cylinders, 25-mL (3)

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 three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 25-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:

- Volatile Acid Voluette® Ampule Standard, 62,500-mg/L as acetic acid
- 500-mL volumetric flask, Class A
- 4-mL volumetric pipet, Class A and pipet filler safety bulb
- Deionized water

1. Prepare a 500 mg/L volatile acids standard solution as follows:
   a. Use a pipet to add 4.00 mL of 62,500-mg/L as acetic acid 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 slight 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 Concentration change per 0.010 Abs change
770	1350 mg/L as acetic acid (HOAC)	1218–1482 mg/L as acetic acid (HOAC)	27 mg/L as acetic acid (HOAC)

Summary of method

The volatile acids test is designed specifically to determine 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. The measurement wavelength is 495 nm for spectrophotometers or 520 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Water, deionized	varies	4 L	27256
Volatile Acid Reagent Set	1	90 tests	2244700
Includes:			
Ethylene Glycol	3 mL	1000 mL	203953
Ferric Chloride-Sulfuric Acid Solution	20 mL	1000 mL	204253
Hydroxylamine Hydrochloride Solution, 100-g/L	1 mL	100 mL	81842

Consumables and replacement items (continued)

Description	Quantity/test	Unit	Item no.
Sodium Hydroxide Standard Solution, 4.5 N	4 mL	1000 mL	204053
Sulfuric Acid Standard Solution, 19.2 N	0.4 mL	1000 mL	203832

Required apparatus

Description	Quantity/test	Unit	Item no.
Centrifuge, 115 VAC, 6 x 15 mL	1	each	2676500
Centrifuge tubes, 15-mL	2	10/pkg	2278739
Centrifuge tube caps	2	20/pkg	2585220
Cylinder, graduated, 10-mL	1	each	50838
Filter paper, folded, 12.5-cm	1	100/pkg	189457
Funnel, poly, 65-mm	1	each	108367
Hot plate, 7 inch x 7 inch, digital, 120 VAC	1	each	2881500
Hot Plate, 7-inch digital, 240 VAC	1	each	2881502
Pipet filler, safety bulb	1	each	1465100
Pipet, serological, 2-mL	1	each	53236
Pipet, volumetric, Class A, 0.5-mL	1	each	1451534
Pipet, volumetric, Class A, 10.00-mL	1	each	1451538
Cell holder assembly	1	each	4788000
Evaporating dish, 125 mm x 65 mm	1	each	2764700
Sample cells, 10-mL square, matched pair	2	2/pkg	2495402

Recommended standards and apparatus

Description	Unit	Item no.
Volatile Acids Standard Solution, 10-mL Voluette® Ampule, 62,500-mg/L as HOAC	16/pkg	1427010
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800

Optional reagents and apparatus

Description	Unit	Item no.
Mixing cylinder, graduated, 25-mL	each	189640
Water bath and rack	each	195555
Pipet, TenSette®, 1.0–10.0 mL	each	1970010
Pipet tips for TenSette® Pipet, 1.0–10.0 mL	250/pkg	2199725
Pipet tips for TenSette® Pipet, 1.0–10.0 mL	50/pkg	2199796
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	1000/pkg	2185628
Flask, volumetric, Class A, 500-mL glass	each	1457449
Finger cots	2/pkg	1464702

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