§ 63.145 Process wastewater provisions - test methods and procedures to determine compliance.

(a) *General.* This section specifies the procedures for performance tests that are conducted to demonstrate compliance of a treatment process or a control device with the control requirements specified in §63.138 of this subpart. Owners or operators conducting a design evaluation shall comply with the requirements of (a)(1) or (a)(2). Owners or operators conducting a performance test shall comply with the applicable requirements in paragraphs (a) through (i) of this section.

(1) *Performance tests and design evaluations for treatment processes.* If design steam stripper option (§63.138(d)) or RCRA option (§63.138(h)) is selected to comply with §63.138, neither a design evaluation nor a performance test is required. For any other non-biological treatment process, the owner or operator shall conduct either a design evaluation as specified in §63.138(j), or a performance test as specified in this section. For closed biological treatment processes, the owner or operator shall conduct either a design evaluation as specified in §63.138(j), or a performance test as specified in this section. For each open biological treatment process, the owner or operator shall conduct a performance test as specified in this section. [Note: Some open biological treatment processes may not require a performance test.

Refer to §63.145(h) and table 36 of this subpart to determine whether the biological treatment process meets the criteria that exempt the owner or operator from conducting a performance test.]

(2) *Performance tests and design evaluations for control devices.* The owner or operator shall conduct either a design evaluation as specified in §63.139(d), or a performance test as specified in paragraph §63.145(i) for control devices other than flares and paragraph §63.145(j) for flares.

(3) *Representative process unit operating conditions.* Compliance shall be demonstrated for representative operating conditions. Operations during periods of startup, shutdown, or malfunction and periods of nonoperation shall not constitute representative conditions. The owner or operator shall record the process information that is necessary to document operating conditions during the test.

(4) *Representative treatment process or control device operating conditions.* Performance tests shall be conducted when the treatment process or control device is operating at a representative inlet flow rate and concentration. If the treatment process or control device will be operating at several different sets of representative operating conditions, the owner or operator shall comply with (4)(i) and (4)(ii) of this paragraph. The owner or operator shall record information that is necessary to document treatment

process or control device operating conditions during the test.

(i) *Range of operating conditions.* If the treatment process or control device will be operated at several different sets of representative operating conditions, performance testing over the entire range is not required. In such cases, the performance test results shall be supplemented with modeling and/or engineering assessments to demonstrate performance over the operating range.

(ii) *Consideration of residence time.* If concentration and/or flow rate to the treatment process or control device are not relatively constant (i.e., comparison of inlet and outlet data will not be representative of performance), the owner or operator shall consider residence time, when determining concentration and flow rate.

(5) *Testing equipment.* All testing equipment shall be prepared and installed as specified in the applicable test methods, or as approved by the Administrator.

(6) *Compounds not required to be considered in performance tests .* Compounds that meet the requirements specified in (a)(6)(i), (a)(6)(ii), or (a)(6)(iii) of this section are not required to be included in the performance test. Concentration measurements based on method 305 shall be adjusted by dividing each concentration by the compound-specific fraction measured (Fm) factor listed in table 34 of this subpart. Concentration measurements based on methods

other than method 305 shall not be adjusted by the compound-specific fraction measured (Fm) factor listed in table 34 of this subpart.

(i) Compounds not used or produced by the chemical manufacturing process unit; or

(ii) Compounds with concentrations at the point of determination that are below 1 part per million by weight; or

(iii) Compounds with concentrations at the point of determination that are below the lower detection limit where the lower detection limit is greater than 1 part per million by weight. The method shall be an analytical method for wastewater which has that compound as a target analyte.

(7) *Treatment using a series of treatment processes.* In all cases where the wastewater provisions in this subpart allow or require the use of a treatment process or control device to comply with emissions limitations, the owner or operator may use multiple treatment processes or control devices, respectively. The owner or operator complying with the requirements of §63.138(a)(7)(i), when wastewater is conveyed by hard-piping, shall comply with either §63.145(a)(7)(i) or §63.145(a)(7)(ii) of this subpart. The owner or operator complying with the requirements of §63.138(a)(7)(ii) of this subpart shall comply with the requirements of §63.145(a)(7)(ii) of this subpart.

(i) The owner or operator shall conduct the performance test across each series of treatment processes. For each series of treatment processes, inlet concentration and flow rate shall be measured either where the wastewater stream enters the first treatment process in a series of treatment processes, or prior to the first treatment process as specified in §63.145(a)(9) of this subpart. For each series of treatment processes, outlet concentration and flow rate shall be measured where the wastewater stream exits the last treatment process in the series of treatment processes, except when the last treatment process is an open or a closed aerobic biological treatment process demonstrating compliance by using the procedures in §63.145(f) or (g) of this subpart. When the last treatment process is either an open or a closed aerobic biological treatment process demonstrating compliance by using the procedures in §63.145(f) or (g) of this subpart, inlet and outlet concentrations and flow rates shall be measured as provided in paragraph (a)(7)(i)(A) and (a)(7)(i)(B) of this section. The mass flow rates removed or destroyed by the series of treatment processes and by the biological treatment process are all used to calculate AMR as specified in §63.145(f)(5)(ii) of this subpart.

(A) The inlet and outlet to the series of treatment processes prior to the biological treatment process are the points at which the wastewater enters the first treatment

process and exits the last treatment process in the series, respectively, except as provided in (a)(9)(ii) of this section.

(B) The inlet to the biological treatment process shall be the point at which the wastewater enters the biological treatment process or the outlet from the series of treatment processes identified in paragraph (a)(7)(i)(A) of this section, except as provided in paragraph (a)(9)(ii) of this section .

(ii) The owner or operator shall conduct the performance test across each treatment process in the series of treatment processes. The mass flow rate removed or destroyed by each treatment process shall be added together to determine whether compliance has been demonstrated using §63.145(c), (d), (e), (f), and (g) of this section, as applicable. If a biological treatment process is one of the treatment processes in the series of treatment processes, the inlet to the biological treatment process shall be the point at which the wastewater enters the biological treatment process, or the inlet to the equalization tank if all the criteria of (a)(9)(ii) of this section are met.

(8) When using a biological treatment process to comply with §63.138 of this subpart, the owner or operator may elect to calculate the actual mass removal (AMR) using a subset of table 8 and/or table 9 compounds determined at the point of determination. All table 8 and/or table 9

compounds measured to determine the RMR, except as provided by §63.145(a)(6), shall be included in the RMR calculation.

(9) The owner or operator determining the inlet for purposes of demonstrating compliance with §63.145 (e), (f), or (g) of this subpart may elect to comply with (a)(9)(i) or (a)(9)(ii) of the section.

(i) When wastewater is conveyed exclusively by hard-piping from the point of determination to a treatment process that is either the only treatment process or the first in a series of treatment processes (i.e., no treatment processes or other waste management units are used upstream of this treatment process to store, handle, or convey the wastewater), the inlet to the treatment process shall be at any location from the point of determination to where the wastewater stream enters the treatment process. When samples are taken upstream of the treatment process and before wastewater streams have converged, the owner or operator shall ensure that the mass flow rate of all Group 1 wastewater streams is accounted for when using §63.138(e) or (f) to comply and that the mass flow rate of all Group 1 and Group 2 wastewater streams is accounted for when using §63.138(g) to comply, except as provided in §63.145(a)(6).

(ii) The owner or operator may consider the inlet to the equalization tank as the inlet to the biological treatment process if all the criteria in paragraphs (a)(9)(ii)(A) through (a)(9)(ii)(C) of this section are met.

The outlet from the series of treatment processes prior to the biological treatment process is the point at which the wastewater exits the last treatment process in the series prior to the equalization tank, if the equalization tank and biological treatment process are part of a series of treatment processes. The owner or operator shall ensure that the mass flow rate of all Group 1 wastewater streams is accounted for when using §63.138(e) or (f) to comply and that the mass flow rate of all Group 1 and Group 2 wastewater streams is accounted for when using §63.138(g) to comply, except as provided in §63.145(a)(6).

(A) The wastewater is conveyed by hard-piping from either the last previous treatment process or the point of determination to the equalization tank.

(B) The wastewater is conveyed from the equalization tank exclusively by hard-piping to the biological treatment process and no treatment processes or other waste management units are used to store, handle, or convey the wastewater between the equalization tank and the biological treatment process.

(C) The equalization tank is equipped with a fixed roof and a closed vent system that routes emissions to a control device that meets the requirements of §63.133(a)(2)(i) and §63.133(b)(1) through (b)(4) of this subpart.

(b) Noncombustion treatment process -- concentration

limits. This paragraph applies to performance tests that are conducted to demonstrate compliance of a noncombustion treatment process with the parts per million by weight wastewater stream concentration limits at the outlet of the treatment process. This compliance option is specifed in § 63.138(b)(1) and § 63.138(c)(1). Wastewater samples shall be collected using sampling procedures which minimize loss of organic compounds during sample collection and analysis and maintain sample integrity per §63.144(b)(5)(ii). Samples shall be collected and analyzed using the procedures specified in §63.144(b)(5)(i), (b)(5)(ii), and (b)(5)(iii) of this subpart. Samples may be grab samples or composite samples. Samples shall be taken at approximately equally spaced time intervals over a 1-hour period. Each 1-hour period constitutes a run, and the performance test shall consist of a minimum of 3 runs. Concentration measurements based on method 305 may be adjusted by dividing each concentration by the compound-specific fraction measured (Fm) factor listed in table 34 of this subpart. Concentration measurements based on methods other than method 305 may be adjusted by multiplying each concentration by the compound-specific fraction measured (Fm) factor listed in table 34 of this subpart. [Note: For wastewater streams that are Group 1 for both table 8 and table 9 compounds, compliance is demonstrated only if the sum of the concentrations of table 9 compounds is less than 50 ppmw,

and the concentration of each table 8 compound is less than 10 ppmw.]

(c) Percent mass removal/destruction option: non-combustion, non-biological treatment process. This paragraph applies to performance tests that are conducted to demonstrate compliance of a noncombustion, non-biological treatment process with the percent mass removal limits specified in §63.138(e)(1) and (2) for table 8 and/or table 9 compounds. The owner or operator shall comply with the requirements specified in §63.145(c)(1) through (c)(5) of this subpart.

(1) *Concentration.* The concentration of table 8 and/or table 9 compounds entering and exiting the treatment process shall be determined as provided in this paragraph. Wastewater samples shall be collected using sampling procedures which minimize loss of organic compounds during sample collection and analysis and maintain sample integrity per §63.144(b)(5)(ii). The method shall be an analytical method for wastewater which has that compound as a target analyte. Samples may be grab samples or composite samples. Samples shall be taken at approximately equally spaced time intervals over a 1-hour period. Each 1-hour period constitutes a run, and the performance test shall consist of a minimum of 3 runs. Concentration measurements based on method 305 shall be adjusted by dividing each concentration by the compound-specific fraction measured (Fm) factor

listed in table 34 of this subpart. Concentration measurements based on methods other than method 305 shall not adjust by the compound-specific fraction measured (Fm) factor listed in table 34 of this subpart.

(2) *Flow rate.* The flow rate of the entering and exiting wastewater streams shall be determined using inlet and outlet flow meters, respectively. Where the outlet flow is not greater than the inlet flow, a flow meter shall be used, and may be used at either the inlet or outlet. Flow rate measurements shall be taken at the same time as the concentration measurements.

(3) *Calculation of mass flow rate -- for noncombustion, nonbiological treatment processes.* The mass flow rates of table 8 and/or table 9 compounds entering and exiting the treatment process are calculated as follows.

(Eqn WW1)

$$QMW_a = \frac{\rho}{p * 10^6} \left(\sum_{k=1}^{p} Q_{a,k} C_{T,a,k} \right)$$

(Eqn WW2)

$$QMW_b = \frac{\rho}{p * 10^6} \left(\sum_{k=1}^{p} Q_{b,k} C_{T,b,k} \right) \qquad \text{(Eqn WW2)}$$

where:

QMW_a, QMW_b = Mass flow rate of table 8 or table 9 compounds, average of all runs, in wastewater entering (QMW_a) or exiting (QMW_b) the treatment process, kilograms per hour.

ρ = Density of the wastewater, kilograms per cubic meter.

$Q_{a,k}$, $Qb_{b,k}$ = Volumetric flow rate of wastewater entering ($Q_{a,k}$) or exiting ($Q_{b,k}$) the treatment process during each run k, cubic meters per hour.

$C_{T,a,k}$, $C_{T,b,k}$ = Total concentration of table 8 or table 9 compounds in wastewater entering ($C_{T,a,k}$) or exiting ($C_{T,b,k}$) the treatment process during each run k, parts per million by weight.

p = Number of runs.

k = Identifier for a run.

10^6 = conversion factor, mg/kg

(4) *Percent removal calculation for mass flow rate.* The percent mass removal across the treatment process shall be calculated as follows:

$$E = \frac{QMW_a - QMW_b}{QMW_a} \times 100 \qquad \text{(Eqn WW3)}$$

where:

E = Removal or destruction efficiency of the treatment process, percent.

QMW_a, QMW_b = Mass flow rate of table 8 or table 9 compounds in wastewater entering (QMW_a) and exiting (QMW_b) the treatment process, kilograms per hour (as calculated using Equations WW1 and WW2).

(5) *Compare mass removal efficiency to required efficiency.* Compare the mass removal efficiency (calculated in Equation WW 3) to the required efficiency as specified in §63.138(e) of this subpart. If complying with §63.138(e)(1), compliance is demonstrated if the mass removal efficiency is 99 percent or greater. If complying with §63.138(e)(2), compliance is demonstrated if the mass removal efficiency is greater than or equal to the flow-weighted average of the fraction removal (Fr) values listed in table 9 of this subpart.

(d) Combustion treatment processes: percent mass removal/destruction option. This paragraph applies to performance tests that are conducted to demonstrate compliance of a combustion treatment process with the percent mass destruction limits specified in §63.138(e)(1) and (2) for table 9 compounds, and/or §63.138(e)(1) for table 8 compounds. The owner or operator shall comply with

the requirements specified in §63.145(d)(1) through (d)(9) of this subpart. [Note: Wastewater streams that are Group 1 for both table 8 and table 9 compounds need only do the compliance demonstration for table 9 compounds.]

(1) *Concentration in wastewater stream entering the combustion treatment process.* The concentration of table 8 and/or table 9 compounds entering the treatment process shall be determined as provided in this paragraph. Wastewater samples shall be collected using sampling procedures which minimize loss of organic compounds during sample collection and analysis and maintain sample integrity per §63.144(b)(5)(ii). The method shall be an analytical method for wastewater which has that compound as a target analyte. Samples may be grab samples or composite samples. Samples shall be taken at approximately equally spaced time intervals over a 1-hour period. Each 1-hour period constitutes a run, and the performance test shall consist of a minimum of 3 runs. Concentration measurements based on Method 305 of Appendix A of this part shall be adjusted by dividing each concentration by the compound-specific fraction measured (Fm) factor listed in table 34 of this subpart. Concentration measurements based on methods other than Method 305 shall not adjust by the compound-specific fraction measured (Fm) factor listed in table 34 of this subpart.

(2) *Flow rate of wastewater entering the combustion*

treatment process. The flow rate of the wastewater stream entering the combustion treatment process shall be determined using an inlet flow meter. Flow rate measurements shall be taken at the same time as the concentration measurements.

(3) *Calculation of mass flow rate in wastewater stream entering combustion treatment processes.* The mass flow rate of table 8 and/or table 9 compounds entering the treatment process is calculated as follows:

$$QMW_a = \frac{\rho}{p * 10^6}\left(\sum_{k=1}^{p} Q_{a,k} * C_{T,a,k}\right) \qquad \text{(Eqn WW4)}$$

where:

QMW_a = Mass flow rate of table 8 or table 9 compounds entering the combustion unit, kilograms per hour.

ρ = Density of the wastewater stream, kilograms per cubic meter.

$Q_{a,k}$ = Volumetric flow rate of wastewater entering the combustion unit during run k, cubic meters per hour.

$C_{T,a,k}$ = Total concentration of table 8 or table 9 compounds in the wastewater stream entering the combustion unit during run k, parts per million by weight.

p = Number of runs.

k = Identifier for a run.

(4) *Concentration in vented gas stream exiting the combustion treatment process.* The concentration of table 8 and/or table 9 compounds exiting the combustion treatment process in any vented gas stream shall be determined as provided in this paragraph. Samples may be grab samples or composite samples. Samples shall be taken at approximately equally spaced time intervals over a 1-hour period. Each 1-hour period constitutes a run, and the performance test shall consist of a minimum of 3 runs. Concentration measurements shall be determined using Method 18 of 40 CFR part 60, appendix A. Alternatively, any other test method validated according to the procedures in Method 301 of appendix A of this part may be used.

(5) *Volumetric flow rate of vented gas stream exiting the combustion treatment process*. The volumetric flow rate of the vented gas stream exiting the combustion treatment process shall be determined using Method 2, 2A, 2C, or 2D of 40 CFR part 60, appendix A, as appropriate. Volumetric flow rate measurements shall be taken at the same time as the concentration measurements.

(6) *Calculation of mass flow rate of vented gas stream exiting combustion treatment processes.* The mass flow rate of table 8 and/or table 9 compounds in a vented gas stream exiting the combustion treatment process shall be

calculated as follows:

$$QMG_a = K_2 \left(\sum_{i=1}^{n} CG_{a,i}\, MW_i \right) QG_a \qquad \text{(Eqn WW5)}$$

$$QMG_b = K_2 \left(\sum_{i=1}^{n} CG_{b,i}\, MW_i \right) QG_b \qquad \text{(Eqn WW6)}$$

where:

$CG_{a,i}$, $CG_{b,i}$ = Concentration of TOC (minus methane and ethane) or total organic HAP, in vented gas stream, entering ($CG_{a,i}$) and exiting ($CG_{b,i}$) the control device, dry basis, parts per million by volume.

QMG_a, QMG_b = Mass rate of TOC (minus methane and ethane) or total organic HAP, in vented gas stream, entering (QMG_a) and exiting (QMG_b) the control device, dry basis, kilograms per hour.

MW_i = Molecular weight of a component , kilogram/kilogram-mole.

QG_a,QG_b = Flow rate of gas stream entering (QG_a) and exiting (QG_b) the control device, dry standard cubic meters per hour .

K_2 = Constant, 41.57×10^{-9} (parts per million)$^{-1}$ (gram-mole per standard cubic meter) (kilogram/gram), where standard temperature (gram-mole per standard cubic meter) is 20 ^{o}C.

i = Identifier for a compound.

n = Number of components in the sample.

(7) *Destruction efficiency calculation.* The destruction efficiency of the combustion unit for table 8 or table 9 compounds shall be calculated as follows:

(Eqn WW7)

$$E = \frac{QMW_a - QMG_b}{QMW_a} * 100$$

where:

E = Destruction efficiency of table 8 or table 9 compounds for the combustion unit, percent.

QMW_a = Mass flow rate of table 8 or table 9 compounds entering the combustion unit, kilograms per hour.

QMG_b = Mass flow rate of table 8 or table 9 compounds in vented gas stream exiting the combustion treatment process, kilograms per hour.

(8) Calculate flow-weighted average of Fr values. Use equation WW8 to calculate the flow-weighted average of the

fraction removal (Fr) values listed in table 9 of this subpart.

(Equ WW8)

$$Fr_{avg} = \frac{\sum_{i=1}^{n}\sum_{k=1}^{p} Fr_i * C_{i,a,k} * Q_{a,k}}{\sum_{k=1}^{p}\sum_{i=1}^{n} C_{i,a,k} * Q_{a,k}}$$

where:

Fr_{avg} = Flow-weighted average of the fraction removal (Fr) values.

$C_{i,a,k}$ = Concentration of table 8 and\or table 9 compounds in wastewater stream entering the combustion unit, during run k, parts per million by weight.

$Q_{a,k}$ = Volumetric flow rate of wastewater entering the combustion unit during run k, cubic meters per hour.

Fr_i = Compound-specific Fr value listed in table 9.

(9) *Calculate flow-weighted average of Fr values and compare to mass destruction efficiency.* Compare the mass destruction efficiency (calculated in Equation WW 7) to the required efficiency as specified in §63.138(e). If complying with §63.138(e)(1), compliance is demonstrated if the mass destruction efficiency is 99 percent or greater. If complying with §63.138(e)(2), compliance is demonstrated

if the mass destruction efficiency is greater than or equal to the flow-weighted average of the fraction removal (Fr) value calculated in equation WW8.

(e) Non-combustion treatment processes including closed biological treatment processes: required mass removal (RMR) option. This paragraph applies to performance tests for non-combustion treatment processes other than open biological treatment processes to demonstrate compliance with the mass removal provisions for table 8 and/or table 9 compounds. Compliance options for noncombustion treatment processes are specified in §63.138(f) of this subpart. Compliance options for closed aerobic or anaerobic biological treatment processes are specified in §63.138(f) and §63.138(g) of this subpart. When complying with §63.138(f), the owner or operator shall comply with the requirements specified in §63.145(e)(1) through (e)(6) of this subpart. When complying with §63.138(g), the owner or operator shall comply with the requirements specified in §63.145(e)(1), (e)(2), (e)(4), (e)(5), and (e)(6) of this subpart. [Note: Wastewater streams that are Group 1 for both table 8 and table 9 compounds need only do the compliance demonstration for table 9 compounds.]

(1) *Concentration in wastewater stream .* The concentration of table 8 and/or table 9 compounds shall be determined as provided in this paragraph. Concentration measurements to determine RMR shall be taken at the point of

determination. Concentration measurements to determine AMR shall be taken at the inlet and outlet to the treatment process and as provided in §63.145(a)(7) for a series of treatment processes. Wastewater samples shall be collected using sampling procedures which minimize loss of organic compounds during sample collection and analysis and maintain sample integrity per §63.144(b)(5)(ii). The method shall be an analytical method for wastewater which has that compound as a target analyte. Samples may be grab samples or composite samples. Samples shall be taken at approximately equally spaced time intervals over a 1-hour period. Each 1-hour period constitutes a run, and the performance test shall consist of a minimum of 3 runs. Concentration measurements based on method 305 shall be adjusted by dividing each concentration by the compound-specific fraction measured (Fm) factor listed in table 34 of this subpart. Concentration measurements based on methods other than method 305 shall not adjust by the compound-specific fraction measured (Fm) factor listed in table 34 of this subpart.

(2) *Flow rate.* Flow rate menasurements to determine RMR shall be taken at the point of determination. Flow rate measurements to determine AMR shall be taken at the inlet and outlet to the treatment process and as provided in §63.145(a)(7) for a series of treatment processes. Flow rate shall be determined using inlet and outlet flow

measurement devices Where the outlet flow is not greater than the inlet flow, a flow measurement device shall be used, and may be used at either the inlet or outlet. Flow rate measurements shall be taken at the same time as the concentration measurements.

(3) *Calculation of required mass removal for non-combustion treatment processes including closed biological treatment processes when using §63.138(f) to comply.* The required mass removal of table 8 and/or table 9 compounds for each Group 1 wastewater stream shall be calculated using the following equation:

(Eqn WW9)

$$RMR = \frac{\rho}{10^9} Q \sum_{i=1}^{n} (C_i * Fr_i)$$

where:

RMR = Required mass removal for treatment process or series of treatment processes, kilograms per hour.

ρ = Density of the Group 1 wastewater stream, kilograms per cubic meter.

Q = Volumetric flow rate of wastewater stream at the point of determination, liters per hour.

i = Identifier for a compound.

n = Number of table 8 or table 9 compounds in stream.

C_i = Concentration of table 8 or table 9 compounds at the point of determination, parts per million by weight.

Fr_i = Fraction removal value of a table 8 or table 9 compound. Fr values are listed in table 9 of this subpart.

10^9 = Conversion factor, mg/kg * l/m^3.

(4) The required mass removal is calculated by adding together the required mass removal for each Group 1 wastewater stream to be combined for treatment when complying with §63.138(f). The required mass removal is 95 percent of the mass flow rate for all Group 1 and Group 2 wastewater streams combined for treatment when complying with §63.138(g).

(5) *Actual mass removal calculation procedure for non-combustion treatment processes including closed biological treatment processes.* The actual mass removal shall be calculated as follows:

(Eqn WW10)

$$AMR = (QMW_a - QMW_b)$$

where:

AMR = Actual mass removal of table 8 or table 9 compounds achieved by treatment process or series of treatment processes, kilograms per hour.

QMW_a = Mass flow rate of table 8 or table 9

compounds in wastewater entering the treatment process or first treament process in a series of treatment processes, kilograms per hour.

QMW_b = Mass flow rate of table 8 or table 9 compounds in wastewater exiting the last treament process in a series of treatment processes, kilograms per hour.

(6) *Compare RMR to AMR.* When complying with §63.138(f), compare the required mass removal (RMR) calculated in equation WW9 to the actual mass removal (AMR) calculated in equation WW10. When complying with §63.138(g), compare the AMR to 95 percent. Compliance is demonstrated if the AMR is greater than or equal to the RMR.

(f) *Open or closed aerobic biological treatment processes: Required mass removal (RMR) option.* This paragraph applies to the use of performance tests that are conducted for open or closed aerobic biological treatment processes to demonstrate compliance with the mass removal provisions for table 8 and/or table 9 compounds. These compliance options are specified in §63.138(f) of this subpart. The owner or operator shall comply with the requirements specified in §63.145(f)(1) through (f)(6) of this subpart. Some compounds may not require a performance test. Refer to §63.145(h) and table 36 of this subpart to determine which compounds may be exempt from the

requirements of this paragraph.

(1) *Concentration in wastewater stream.* The concentration of table 8 and/or table 9 compounds shall be determined as provided in this paragraph. Concentration measurements to determine RMR shall be taken at the point of determination. Concentration measurements to determine AMR shall be taken at the inlet and outlet to the treatment process and as provided in §63.145(a)(7) for a series of treatment processes. Wastewater samples shall be collected using sampling procedures which minimize loss of organic compounds during sample collection and analysis and maintain sample integrity per §63.144(b)(5)(ii). The method shall be an analytical method for wastewater which has that compound as a target analyte. Samples may be grab samples or composite samples. Samples shall be taken at approximately equally spaced time intervals over a 1-hour period. Each 1-hour period constitutes a run, and the performance test shall consist of a minimum of 3 runs. Concentration measurements based on method 305 shall be adjusted by dividing each concentration by the compound-specific fraction measured (Fm) factor listed in table 34 of this subpart. Concentration measurements based on methods other than method 305 shall not adjust by the compound-specific fraction measured (Fm) factor listed in table 34 of this subpart.

(2) *Flow rate.* Flow rate menasurements to determine

RMR shall be taken at the point of determination. Flow rate measurements to determine AMR shall be taken at the inlet and outlet to the treatment process and as provided in §63.145(a)(7) for a series of treatment processes. Flow rate shall be determined using inlet and outlet flow measurement devices. Where the outlet flow is not greater than the inlet flow, a flow measurement device shall be used, and may be used at either the inlet or outlet. Flow rate measurements shall be taken at the same time as the concentration measurements.

(3) *Calculation of required mass removal for open or closed aerobic biological treatment processes.* The required mass removal of table 8 and/or table 9 compounds for each Group 1 wastewater stream shall be calculated using the following equation:

(Eqn WW11)

$$RMR = \frac{\rho}{10^9} Q \sum_{i=1}^{n} (C_i * Fr_i)$$

where:

RMR = Required mass removal for treatment process or series of treatment processes, kilograms per hour.

ρ = Density of the Group 1 wastewater stream, kilograms per cubic meter.

Q = Volumetric flow rate of wastewater stream at the point of determination, liters per hour.

i = Identifier for a compound.

n = Number of table 8 or table 9 compounds in stream.

C_i = Concentration of table 8 or table 9 compounds at the point of determination, parts per million by weight.

Fr_i = Fraction removal value of a table 8 or table 9 compound. Fr values are listed in table 9 of this subpart.

10^9 = Conversion factor, mg/kg * l/m^3.

(4) The required mass removal is calculated by adding together the required mass removal for each Group 1 wastewater stream to be combined for treatment.

(5) *Actual mass removal calculation procedure for open or closed aerobic biological treatment processes.* The actual mass removal (AMR) shall be calculated as specified in paragraph (f)(1)(i) of this section when the performance test is performed across the open or closed aerobic biological treatment process only. When wastewater is not conveyed by hard-piping, AMR shall be calculated as specified in §63.145(f)(5)(i) and the requirements of §63.145(a)(7)(i) are met. When combinations of treatment processes are used to comply with §63.138, AMR shall be calculated as specified in paragraph (f)(5)(ii) of this section when conveyance is by hard-piping and the requirements of §63.145(a)(7)(i) are met.

(i) Calculate AMR for the open or closed aerobic biological treatment process as follows:

(Eqn WW12)

$$AMR = QMW_a * F_{bio}$$

AMR = Actual mass removal of table 8 or table 9 compounds achieved by treatment process, kilograms per hour.

QMW_a = Mass flow rate of table 8 or table 9 compounds in wastewater entering the treatment process, kilograms per hour.

F_{bio} = Site-specific fraction of table 8 or table 9 compounds biodegraded. F_{bio} shall be determined as specified in §63.145(h) and appendix C of this subpart.

(ii) Calculate AMR for a series of treatment units where the last treatment unit is an open or closed aerobic biological treatment process as follows:

(Eqn WW13)

$$AMR = QMW_a - (QMW_b)(1 - F_{bio})$$

where:

AMR = Actual mass removal of table 8 or table 9 compounds achieved by treatment process or series of treatment processes, kilograms per hour.

QMW_a = Mass flow rate of table 8 or table 9 compounds in wastewater entering the first treament process in a series of treatment processes, kilograms per hour.

QMW_b = Mass flow rate of table 8 or table 9 compounds in wastewater exiting the last treatment process in a series of treatment processes prior to the biological treatment process, kilograms per hour.

F_{bio} = Site-specific fraction of table 8 or table 9 compounds biodegraded. F_{bio} shall be determined as specified in §63.145(h) and appendix C of this subpart.

(6) *Compare RMR to AMR.* Compare the required mass removal (RMR) calculated in equation WW11 to the actual mass removal calculated in either equation WW12 or WW13, as applicable. Compliance is demonstrated if the AMR is greater than or equal to the RMR.

(g) *Open or closed aerobic biological treatment processes: 95 percent mass removal option.* This paragraph applies to performance tests that are conducted for open or closed aerobic biological treatment processes to demonstrate compliance with the 95 percent mass removal provisions for table 8 and/or table 9 compounds. This compliance option is specified in §63.138(g) of this subpart. The RMR for this option is 95 percent mass removal. The owner or operator

shall comply with the requirements specified in §63.145(g)(1) to determine AMR and (g)(2) of this subpart to determine whether compliance has been demonstrated. Some compounds may not require a performance test. Refer to §63.145(h) and table 36 of this subpart to determine which compounds may be exempt from the requirements of this paragraph. [Note: Wastewater streams that are Group 1 for both table 8 and table 9 compounds need only do the compliance demonstration for table 9 compounds.]

(1) The owner or operator shall comply with the requirements specified in §63.145(f)(1) through §63.145(f)(5) of this subpart to determine actual mass removal (AMR). References to Group 1 wastewater streams shall be deemed Group 1 and Group 2 wastewater streams for the purposes of this paragraph.

(2) *Compare RMR to AMR.* Compliance is demonstrated if the AMR is greater than or equal 95 percent.

(h) *Site-specific fraction biodegraded (Fbio).* The compounds listed in table 9 of this subpart are divided into three sets for the purpose of determining whether Fbio must be determined, and if Fbio must be determined, which procedures may be used to determine compound-specific kinetic parameters. These sets are designated as lists 1, 2, and 3 in table 36 of this subpart.

(1) *Performance test exemption*. If a biological treatment process meets the requirements specified in

paragraphs (h)(1)(i) and (h)(1)(ii) of this section, the owner or operator is not required to determine Fbio and is exempt from the applicable performance test requirements specified in §63.138 of this subpart.

(i) The biological treatment process meets the definition of "enhanced biological treatment process" in §63.111 of this subpart.

(ii) At least 99 percent by weight of all compounds on table 36 of this subpart that are present in the aggregate of all wastewater streams using the biological treatment process to comply with §63.138 of this subpart are compounds on list 1 of table 36 of this subpart.

(2) *Fbio determination*. For wastewater streams that include one or more compounds on lists 2 and/or 3 of table 36 of this subpart that do not meet criteria in paragraph (h)(1)(ii) of this section, the owner or operator shall determine Fbio for the biological treatment process using the procedures in Appendix C to part 63, and paragraph (h)(2)(i) or (h)(2)(ii) of this section. For biological treatment processes that do not meet the definition for enhanced biological treatment in §63.111 of this subpart, the owner or operator shall determine the Fbio for the biological treatment process using any of the procedures in Appendix C to part 63, except the batch tests procedure.

(i) *Wastewater streams without list 3 compounds that are treated in enhanced biological treatment processes.* For

wastewater streams that include no compounds on list 3 of table 36 of this subpart and the biological treatment process meets the definition of enhanced biological treatment in §63.111 of this subpart, the owner or operator shall determine Fbio for the list 2 compounds using any of the procedures specified in Appendix C of 40 CFR part 63. The owner or operator shall calculate Fbio for the list 1 compounds using the defaults for first order biodegradation rate constants (K_1) in table 37 of subpart G and follow the procedure explained in Form IIA of Appendix C, 40 CFR part 63, or any of the procedures specified in Appendix C, 40 CFR part 63.

(ii) *Wastewater streams with list 3 compounds that are treated in enhanced biological treatment processes.* For wastewater streams that include one or more compounds on list 3 of table 36 of this subpart, the owner or operator shall determine Fbio for the list 3 compounds using any of the procedures specified in Appendix C, 40 CFR part 63, except the batch tests procedure. The owner or operator shall determine Fbio for the list 2 compounds using any of the procedures specified in Appendix C 40 CFR part 63. The owner or operator shall calculate Fbio for the list 1 compounds using the defaults for first order biodegradation rate constants (K_1) in table 37 of subpart G and follow the procedure explained in Form IIA of Appendix C 40 CFR part 63, or any of the procedures specified in Appendix C of 40

CFR part 63.

(i) *Performance tests for control devices other than flares.* This paragraph applies to performance tests that are conducted to demonstrate compliance of a control device with the efficiency limits specified in §63.139(c). If complying with the 95 percent reduction efficiency requirement, comply with the requirements specified in paragraphs (i)(1) through (i)(9) of this section. If complying with the 20 ppm by volume requirement, comply with the requirements specified in paragraphs (i)(1) through (i)(6) and (i)(9) of this section. The 20 ppm by volume limit or 95 percent reduction efficiency requirement shall be measured as either total organic HAP or as TOC minus methane and ethane.

(1) *Sampling sites.* Sampling sites shall be selected using Method 1 or 1A of 40 CFR part 60, appendix A, as appropriate. For determination of compliance with the 95 percent reduction requirement, sampling sites shall be located at the inlet and the outlet of the control device. For determination of compliance with the 20 parts per million by volume limit, the sampling site shall be located at the outlet of the control device.

(2) *Concentration in gas stream entering or exiting the control device.* The concentration of total organic HAP or TOC in a gas stream shall be determined as provided in this paragraph. Samples may be grab samples or composite

samples (i.e., integrated samples). Samples shall be taken at approximately equally spaced time intervals over a 1-hour period. Each 1-hour period constitutes a run, and the performance test shall consist of a minimum of 3 runs. Concentration measurements shall be determined using Method 18 of 40 CFR part 60, appendix A. Alternatively, any other test method validated according to the procedures in Method 301 of appendix A of this part may be used.

(3) *Volumetric flow rate of gas stream entering or exiting the control device*. The volumetric flow rate of the gas stream shall be determined using Method 2, 2A, 2C, or 2D of 40 CFR part 60, appendix A, as appropriate. Volumetric flow rate measurements shall be taken at the same time as the concentration measurements.

(4) *Calculation of TOC concentration.* The TOC concentration (CG_T) is the sum of the concentrations of the individual components. If compliance is being determined based on TOC, the owner or operator shall compute TOC for each run using the following equation:

(Eqn WW14)

$$CG_T = \frac{1}{m}\sum_{j=1}^{m}\left(\sum_{i=1}^{n} CGS_{i,j}\right)$$

where:

CG_T = Total concentration of TOC (minus methane and

ethane) in vented gas stream, average of samples, dry basis, parts per million by volume.

$CGS_{i,j}$ = Concentration of sample components in vented gas stream for sample j, dry basis, parts per million by volume.

i = Identifier for a compound.

n = Number of components in the sample.

j = Identifier for a sample.

m = Number of samples in the sample run.

(5) *Calculation of total organic HAP concentration.* The owner or operator determining compliance based on total organic HAP concentration (C_{HAP}) shall compute C_{HAP} according to the equation WW14, except that only table 9 compounds shall be summed.

(6) *Percent oxygen correction for combustion control devices.* If the control device is a combustion device, comply with the requirements specified in paragraph (i)(6)(i) to determine oxygen concentration , and in paragraph (i)(6)(ii) to calclulate the percent oxygen correction.

(i) *Oxygen concentration.* The concentration of TOC or total organic HAP shall be corrected to 3 percent oxygen if the control device is a combustion device. The emission rate correction factor for excess air, composite sampling (i.e., integrated sampling) and analysis procedures of

Method 3B of 40 CFR part 60, appendix A shall be used to determine the actual oxygen concentration ($\%0_{2d}$). The samples shall be taken during the same time that the TOC (minus methane or ethane) or total organic HAP samples are taken.

(ii) *3 percent oxygen calculation.* The concentration corrected to 3 percent oxygen (CG_C), when required, shall be computed using the following equation:

(Eqn WW15)

$$CG_C = CG_T \left(\frac{17.9}{20.9 - \%O_{2d}} \right)$$

where:

CG_C = Concentration of TOC or organic HAP corrected to 3 percent oxygen, dry basis, parts per million by volume.

CG_T = Total concentration of TOC (minus methane and ethane) in vented gas stream, average of samples, dry basis, parts per million by volume.

$\%0_{2d}$ = Concentration of oxygen measured in vented gas stream, dry basis, percent by volume.

(7) *Mass rate calculation.* The mass rate of either TOC (minus methane and ethane) or total organic HAP shall be calculated using the following equations. Where the mass

rate of TOC is being calculated, all organic compounds (minus methane and ethane) measured by methods specified in (i)(2) of this section are summed using equations WW16 and WW17. Where the mass rate of total organic HAP is being calculated, only table 9 compounds shall be summed using equations WW16 and WW17.

$$QMG_a = K_2 \left(\sum_{i=1}^{n} CG_{a,i} \, MW_i \right) QG_a \qquad \text{(Eqn WW16)}$$

$$QMG_b = K_2 \left(\sum_{i=1}^{n} CG_{b,i} \, MW_i \right) QG_b$$

where:

$CG_{a,i}$, $CG_{b,i}$ = Concentration of TOC (minus methane and ethane) or total organic HAP, in vented gas stream, entering ($CG_{a,i}$) and exiting ($CG_{b,i}$) the control device, dry basis, parts per million by volume.

QMG_a, QMG_b = Mass rate of TOC (minus methane and ethane) or total organic HAP, in vented gas stream, entering (QMG_a) and exiting (QMG_b) the control

device, dry basis, kilograms per hour.

MW_i = Molecular weight of a component , kilogram/kilogram-mole.

QG_a,QG_b = Flow rate of gas stream entering (QG_a) and exiting (QG_b) the control device, dry standard cubic meters per hour .

K_2 = Constant, 41.57×10^{-9} (parts per million)$^{-1}$ (gram-mole per standard cubic meter) (kilogram/gram), where standard temperature (gram-mole per standard cubic meter) is 20 ^{o}C.

i = Identifier for a compound.

n = Number of components in the sample.

(8) *Percent reduction calculation.* The percent reduction in TOC (minus methane and ethane) or total organic HAP shall be calculated as follows:

(Eqn WW18)

$$E = \frac{QMG_a - QMG_b}{QMG_a} (100\%)$$

where:

E = Destruction efficiency of control device, percent.

QMG_a,QMG_b = Mass rate of TOC (minus methane and ethane) or total organic HAP, in vented

gas stream entering and exiting (QMG_b) the control device, dry basis, kilograms per hour.

(9) *Compare mass destruction efficiency to required efficiency.* Compliance is demonstrated if the mass destruction efficiency (calculated in equation WW18) is 95 percent or greater.

(j) *Compliance demonstration for flares.* When a flare is used to comply with §63.139 (c) of this subpart, the owner or operator shall comply with the flare provisions in §63.11(b) of subpart A.

(1) The compliance determination required by §63.6(h) of subpart A shall be conducted using Method 22 of 40 CFR part 60, appendix A, to determine visible emissions.

(2) An owner or operator is not required to conduct a performance test to determine percent emission reduction or outlet organic HAP or TOC concentration when a flare is used.

33. The tables in the appendix to subpart G are amended by revising tables 3,4, 11 and 12; removing and reserving tables 14a and 14b; revising tables 15a and 15b; removing and reserving table 16; revising tables 17, 18, and 34; and adding tables 35, 36, and 37 and figure 1 to read as follows:

TABLE 3. PROCESS VENTS -- MONITORING, RECORDKEEPING, AND REPORTING REQUIREMENTS FOR COMPLYING WITH 98 WEIGHT-PERCENT REDUCTION OF TOTAL ORGANIC HAP EMISSIONS OR A LIMIT OF 20 PARTS PER MILLION BY VOLUME

Control Device	Parameters to be Monitored[a]	Recordkeeping and Reporting Requirements for Monitored Parameters
Thermal Incinerator	Firebox temperature[b] [63.114(a)(1)(i)]	1. Continuous records[c] 2. Record and report the firebox temperature averaged over the full period of the performance test - NCS[d] 3. Record the daily average firebox temperature for each operating day[e] 4. Report all daily average temperatures that are outside the range established in the NCS or operating permit and all operating days when insufficient monitoring data are collected[f] - PR[g]
Catalytic Incinerator	Temperature upstream and downstream of the catalyst bed [63.114(a)(1)(ii)]	1. Continuous records 2. Record and report the upstream and downstream temperatures and the temperature difference across the catalyst bed averaged over the full period of the performance test - NCS 3. Record the daily average upstream temperature and temperature difference across catalyst bed for each operating day[e] 4. Report all daily average upstream temperatures that are outside the range established in the NCS or operating permit - PR 5. Report all daily average temperature differences across the catalyst bed that are outside the range established in the NCS or operating permit - PR 6. Report all operating days when insufficient monitoring data are collected[f]

TABLE 3. PROCESS VENTS -- MONITORING, RECORDKEEPING, AND REPORTING REQUIREMENTS FOR COMPLYING WITH 98 WEIGHT-PERCENT REDUCTION OF TOTAL ORGANIC HAP EMISSIONS OR A LIMIT OF 20 PARTS PER MILLION BY VOLUME (CONTINUED)

Control Device	Parameters to be Monitored[a]	Recordkeeping and Reporting Requirements for Monitored Parameters
Boiler or Process Heater with a design heat input capacity less than 44 megawatts and Vent Stream is not introduced with or as the primary fuel	Firebox temperature[b] [63.114(a)(3)]	1. Continuous records 2. Record and report the firebox temperature averaged over the full period of the performance test - NCS 3. Record the daily average firebox temperature for each operating day[e] 4. Report all daily average firebox temperatures that are outside the range established in the NCS or operating permit and all operating days when insufficient monitoring data are collected[f] - PR
Flare	Presence of a flame at the pilot light [63.114(a)(2)]	1. Hourly records of whether the monitor was continuously operating and whether the pilot flame was continuously present during each hour 2. Record and report the presence of a flame at the pilot light over the full period of the compliance determination - NCS 3. Record the times and durations of all periods when a pilot flame is absent or the monitor is not operating 4. Report the times and durations of all periods when all pilot flames of a flare are absent - PR

TABLE 3. PROCESS VENTS -- MONITORING, RECORDKEEPING, AND REPORTING REQUIREMENTS FOR COMPLYING WITH 98 WEIGHT-PERCENT REDUCTION OF TOTAL ORGANIC HAP EMISSIONS OR A LIMIT OF 20 PARTS PER MILLION BY VOLUME (CONTINUED)

Control Device	Parameters to be Monitored[a]	Recordkeeping and Reporting Requirements for Monitored Parameters
Scrubber for Halogenated Vent Streams (Note: Controlled by a combustion device other than a flare)	pH of scrubber effluent [63.114(a)(4)(i)], and	1. Continuous records 2. Record and report the pH of the scrubber effluent averaged over the full period of the performance test - NCS 3. Record the daily average pH of the scrubber effluent for each operating day[e] 4. Report all daily average pH values of the scrubber effluent that are outside the range established in the NCS or operating permit and all operating days when insufficient monitoring data are collected[f] - PR
Scrubber for Halogenated Vent Streams (Note: Controlled by a combustion device other than a flare) (Continued)	Scrubber liquid and gas flow rates [63.114(a)(4)(ii)]	1. Continuous records 2. Record and report the scrubber liquid/gas ratio averaged over the full period of the performance test - NCS 3. Record the daily average scrubber liquid/gas ratio for each operating day[e] 4. Report all daily average scrubber liquid/gas ratios that are outside the range established in the NCS or operating permit and all operating days when insufficient monitoring data are collected[f] - PR

TABLE 3. PROCESS VENTS -- MONITORING, RECORDKEEPING, AND REPORTING REQUIREMENTS FOR COMPLYING WITH 98 WEIGHT-PERCENT REDUCTION OF TOTAL ORGANIC HAP EMISSIONS OR A LIMIT OF 20 PARTS PER MILLION BY VOLUME (CONCLUDED)

Control Device	Parameters to be Monitored[a]	Recordkeeping and Reporting Requirements for Monitored Parameters
All Control Devices	Presence of flow diverted to the atmosphere from the control device [63.114(d)(1)] or	1. Hourly records of whether the flow indicator was operating and whether flow was detected at any time during each hour. 2. Record and report the times and durations of all periods when the vent stream is diverted through a bypass line or the monitor is not operating - PR
	Monthly inspections of sealed valves [63.114(d)(2)]	1. Records that monthly inspections were performed 2. Record and report all monthly inspections that show the valves are not closed or the seal has been changed - PR

[a]Regulatory citations are listed in brackets.

[b]Monitor may be installed in the firebox or in the ductwork immediately downstream of the firebox before any substantial heat exchange is encountered.

[c]"Continuous records" is defined in § 63.111 of this subpart.

[d]NCS = Notification of Compliance Status described in § 63.152 of this subpart.

[e]The daily average is the average of all recorded parameter values for the operating day. If all recorded values during an operating day are within the range established in the NCS or operating permit, a statement to this effect can be recorded instead of the daily average.

[f]The periodic reports shall include the duration of periods when monitoring data is not collected for each excursion as defined in § 63.152(c)(2)(ii)(A) of this subpart.

[g]PR = Periodic Reports described in § 63.152 of this subpart.

TABLE 4. PROCESS VENTS -- MONITORING, RECORDKEEPING, AND REPORTING REQUIREMENTS FOR MAINTAINING A TRE INDEX VALUE >1.0 AND ≤4.0

Final Recovery Device	Parameters to be Monitored[a]	Recordkeeping and Reporting Requirements for Monitored Parameters
Absorber[b]	Exit temperature of the absorbing liquid [63.114(b)(1)], and	1. Continuous records[c] 2. Record and report the exit temperature of the absorbing liquid averaged over the full period of the TRE determination - NCS[d] 3. Record the daily average exit temperature of the absorbing liquid for each operating day[e] 4. Report all the daily average exit temperatures of the absorbing liquid that are outside the range established in the NCS or operating permit - PR[f]
	Exit specific gravity [63.114(b)(1)]	1. Continuous records 2. Record and report the exit specific gravity averaged over the full period of the TRE determination - NCS 3. Record the daily average exit specific gravity for each operating day[e] 4. Report all daily average exit specific gravity values that are outside the range established in the NCS or operating permit - PR
Condenser[d]	Exit (product side) temperature [63.114(b)(2)]	1. Continuous records 2. Record and report the exit temperature averaged over the full period of the TRE determination - NCS 3. Record the daily average exit temperature for each operating day[e] 4. Report all daily average exit temperatures that are outside the range established in the NCS or operating permit - PR

(Continued)

TABLE 4. PROCESS VENTS -- MONITORING, RECORDKEEPING, AND REPORTING REQUIREMENTS FOR MAINTAINING A TRE INDEX VALUE >1.0 AND ≤4.0 (CONCLUDED)

Final Recovery Device	Parameters to be Monitored[a]	Recordkeeping and Reporting Requirements for Monitored Parameters
Carbon Adsorber[d]	Total regeneration stream mass flow during carbon bed regeneration cycle(s) [63.114(b)(3)], and	1. Record of total regeneration stream mass flow for each carbon bed regeneration cycle 2. Record and report the total regeneration stream mass flow during each carbon bed regeneration cycle during the period of the TRE determination - NCS 3. Report all carbon bed regeneration cycles when the total regeneration stream mass flow is outside the range established in the NCS or operating permit - PR
	Temperature of the carbon bed after regeneration [and within 15 minutes of completing any cooling cycle(s)] [63.114(b)(3)]	1. Records of the temperature of the carbon bed after each regeneration 2. Record and report the temperature of the carbon bed after each regeneration during the period of the TRE determination - NCS 3. Report all carbon bed regeneration cycles during which temperature of the carbon bed after regeneration is outside the range established in the NCS or operating permit - PR
All Recovery Devices (as an alternative to the above)	Concentration level or reading indicated by an organic monitoring device at the outlet of the recovery device	1. Continuous records 2. Record and report the concentration level or reading averaged over the full period of the TRE determination - NCS 3. Record the daily average concentration level or reading for each operating day[e] 4. Report all daily average concentration levels or readings that are outside the range established in the NCS or operating permit - PR

TABLE 4. PROCESS VENTS -- MONITORING, RECORDKEEPING, AND REPORTING REQUIREMENTS FOR MAINTAINING A TRE INDEX VALUE >1.0 AND ≤4.0 (CONCLUDED)

[a]Regulatory citations are listed in brackets.

[b]Alternatively, these devices may comply with the organic monitoring device provisions listed at the end of this table under "All Recovery Devices."

[c]"Continuous records" is defined in §63.111 of this subpart.

[d]NCS = Notification of Compliance Status described in §63.152 of this subpart.

[e]The daily average is the average of all values recorded during the operating day. If all recorded values during an operating day are within the range established in the NCS or operating permit, a statement to this effect can be recorded instead of the daily average.

[f]PR = Periodic Reports described in §63.152 of this subpart.

TABLE 11. WASTEWATER -- INSPECTION AND MONITORING REQUIREMENTS FOR WASTE MANAGEMENT UNITS

To Comply With	Inspection or Monitoring Requirement	Frequency of Inspection or Monitoring	Method
TANKS:			
63.133(b)(1)	Inspect fixed roof and all openings for leaks	Initially Semi-annually	Visual
63.133(c)	Inspect floating roof in accordance with §§63.120(a)(2) and (a)(3)	See §63.120(a)(2) and (a)(3)	Visual
63.133(d)	Measure floating roof seal gaps in accordance with §§63.120(b)(2)(i) through (b)(4) - Primary seal gaps - Secondary seal gaps	 Once every 5 years Annually	See §63.120(b)(2)(i) through (b)(4)
63.133(f) 63.133(g)	Inspect wastewater tank for control equipment failures and improper work practices	Initially Semi-annually	Visual
SURFACE IMPOUNDMENTS:			
63.134(b)(1) 63.134(b)(1)	Inspect cover and all openings for leaks	Initially Semi-annually	Visual
63.134(c)	Inspect surface impoundment for control equipment failures and improper work practices	Initially Semi-annually	Visual

TABLE 11. WASTEWATER -- INSPECTION AND MONITORING REQUIREMENTS FOR WASTE MANAGEMENT UNITS (CONTINUED)

To Comply With	Inspection or Monitoring Requirement	Frequency of Inspection or Monitoring	Method
CONTAINERS:			
63.135(b)(1) 63.135(b)(2)(ii)	Inspect cover and all openings for leaks	Semi-annually Initially	Visual
63.135(d)(1)	Inspect enclosure and all openings for leaks	Initially Semi-annually	Visual
63.135(e)	Inspect container for control equipment failures and improper work practices	Semi-annually	Visual
INDIVIDUAL DRAIN SYSTEMS[a]:			
63.136(b)(1)	Inspect cover and all openings to ensure there are no gaps, cracks, or holes	Initially Semi-annually	Visual
63.136(c)	Inspect individual drain system for control equipment failures and improper work practices	Semi-annually	Visual
63.136(e)(1)	Verify that sufficient water is present to properly maintain integrity of water seals	Semi-annually	Visual or smoke test or other means as specified
63.136(f)(1)	Inspect all drains using tightly-fitted caps or plugs to ensure caps and plugs are in place and properly installed	Semi-annually	Visual
63.136(f)(2)	Inspect all junction boxes to ensure covers are in place and have no visible gaps, cracks, or holes	Semi-annually	Visual
63.136(f)(3)	Inspect unburied portion of all sewer lines for cracks and gaps	Semi-annually	Visual

TABLE 11. WASTEWATER -- INSPECTION AND MONITORING REQUIREMENTS FOR WASTE MANAGEMENT UNITS (CONTINUED)

To Comply With	Inspection or Monitoring Requirement	Frequency of Inspection or Monitoring	Method
OIL-WATER SEPARATORS:			
63.137(b)(1)	Inspect fixed roof and all openings for leaks	Initially Semi-annually	Visual
63.137(c)	Measure floating roof seal gaps in accordance with 40 CFR 60.696(d)(1)		See 40 CFR 60.696(d)(1)
	- Primary seal gaps	Once every 5 years	
63.137(c)	- Secondary seal gaps	Annually	
63.137(d)	Inspect oil-water separator for control equipment failures and improper work practices	Semi-annually	Visual

aAs specified in §63.136(a), the owner or operator shall comply with either the requirements of §63.136(b) and (c) or §63.136(e) and (f).

TABLE 12. MONITORING REQUIREMENTS FOR TREATMENT PROCESSES

	To Comply With	Parameters to be Monitored	Frequency	Methods
1.	Required mass removal of Table 8 and/or Table 9 compound(s) from wastewater treated in a properly operated biological treatment unit 63.138(f) 63.138(g)	Appropriate parameters as specified in §63.143(c) and approved by permitting authority	Appropriate frequency as approved by permitting authority	Appropriate methods as approved by permitting authority
2.	Design steam stripper 63.138(d)	Steam flow rate	Continuously	Integrating steam flow monitoring device equipped with a continuous recorder
		Wastewater feed mass flow rate	Continuously	Liquid flow meter installed at stripper influent and equipped with a continuous recorder
		Wastewater feed temperature	Continuously	Liquid temperature monitoring device installed at stripper influent and equipped with a continuous recorder
3.	Alternative monitoring parameters	Other parameters may be monitored upon approval from the Administrator in accordance with the requirements specified in §63.143(d)		

Table 14a [Reserved]

Table 14b [Reserved]

TABLE 15. WASTEWATER -- INFORMATION ON TABLE 8 AND/OR TABLE 9 COMPOUNDS TO BE SUBMITTED WITH NOTIFICATION OF COMPLIANCE STATUS FOR PROCESS UNITS AT NEW AND/OR EXISTING SOURCES[a,b]

Process Unit Identification Code[c]	Stream Identification Code	Concentration of Table 8 and/or Table 9 Compound(s) (ppmw)[d,e]	Flow Rate (lpm)[e,f]	Group 1 or Group 2[g]	Compliance Approach[h]	Treatment Process(es) Identification[i]	Waste Management Unit(s) Identification	Intended Control Device

[a]The information specified in this table must be submitted; however, it may be submitted in any format. This table presents an example format.

[b]Other requirements for the Notification of Compliance Status are specified in §63.152(b) of this subpart.

[c]Also include a description of the process unit (e.g., benzene process unit).

[d]Except when §63.132(e) is used, annual average concentration as specified in §63.132(c) or (d) and §63.144.

[e]When §63.132(e) is used, indicate the wastewater stream is a designated Group 1 wastewater stream.

[f]Except when §63.132(e) is used, annual average flow rate as specified in §63.132(c) or (d) and in §63.144.

[g]Indicate whether stream is Group 1 or Group 2. If Group 1, indicate whether it is Group 1 for Table 8 or Table 9 compounds or for both Table 8 and Table 9 compounds.

[h]Cite §63.138 compliance option used.

Table 16 [Reserved]

TABLE 17. INFORMATION FOR TREATMENT PROCESSES TO BE SUBMITTED WITH NOTIFICATION OF COMPLIANCE STATUS[a,b]

Treatment Process Identification[c]	Description[d]	Wastewater Stream(s) Treated[e]	Monitoring Parameters[f]
* * * * *			

* * * * *

[c]Identification codes should correspond to those listed in Table 15.

* * * * *

[e]Stream identification code for each wastewater stream treated by each treatment unit. Identification codes should correspond to entries listed in Table 15.

[f]Parameter(s) to be monitored or measured in accordance with Table 12 and §63.143 of this Subpart.

TABLE 18. INFORMATION FOR WASTE MANAGEMENT UNITS TO BE SUBMITTED WITH NOTIFICATION OF COMPLIANCE STATUS[a,b]

Waste Management Unit Identification[c]	Description[d]	Wastewater Stream(s) Received or Managed[e]

* * * * *

[c]Identification codes should correspond to those listed in Table 15.

* * * * *

[e]Stream identification code for each wastewater stream received or managed by each waste management unit. Identification codes should correspond to entries listed in Tables 15a and 15b.

TABLE 34. FRACTION MEASURED (F_m) AND FRACTION EMITTED (F_e) FOR HAP COMPOUNDS IN WASTEWATER STREAMS

Chemical Name	CAS Number[a]	F_m	F_e
* * * * *			
Chlorobenzene	108907	1.00	0.73
* * * * *			
Isophorone	78591	0.51	0.11
* * * * *			
Trichloroethane (1,1,2-) (Vinyl Trichloride)	79005	1.00	0.60
* * * * *			
Trichlorophenol (2,4,5-)	95954	0.11	0.086
* * * * *			

* * * * *

Table 35. Control Requirements for Items of Equipment That Meet the Criteria of § 63.149 of Subpart G

Item of Equipment	Control Requirement[a]
Drain or drain hub	(a) Tight fitting solid cover (TFSC); or (b) TFSC with a vent to either a process or to a control device meeting the requirements of § 63.139 (c); or (c) Water seal with submerged discharge or barrier to protect discharge from wind.
Manhole[b]	(a) TFSC; or (b) TSFC with a vent to either a process or to a control device meeting the requirements of § 63.139 (c); or (c) If the item is vented to the atmosphere, use a TFSC with a properly operating water seal at the entrance or exit to the item to restrict ventilation in the collection system. The vent pipe shall be at least 90 cm in length and not exceeding 10.2 cm in diameter.
Lift station	(a) TFSC; or (b) TFSC with a vent to either a process, or to a control device meeting the requirements of § 63.139 (c); or (c) If the lift station is vented to the atmosphere, use a TFSC with a properly operating water seal at the entrance or exit to the item to restrict ventilation in the collection system. The vent pipe shall be at least 90 cm in length and not exceeding 10.2 cm in diameter. The lift station shall be level controlled to minimize changes in the liquid level.
Trench	(a) TFSC; or (b) TSFC with a vent to either a process or to a control device meeting the requirements of § 63.139 (c); or (c) If the item is vented to the atmosphere, use a TFSC with a properly operating water seal at the entrance or exit to the item to restrict ventilation in the collection system. The vent pipe shall be at least 90 cm in length and not exceeding 10.2 cm in diameter.

Table 35. Control Requirements for Items of Equipment That Meet the Criteria of § 63.149 of Subpart G

Item of Equipment	Control Requirement[a]
Pipe	Each pipe shall have no visible gaps in joints, seals, or other emission interfaces.
Oil/Water separator	(a) Equip with a fixed roof and closed vent system that routes vapors to process equipment or to a control device meeting the requirements of § 63.139 (c); or (b) Equip with a floating roof that meets the equipment specifications of § 60.693 (a)(1)(i), (a)(1)(ii), (a)(2), (a)(3), and (a)(4).
Tank[c]	Maintain a fixed roof[d]. If the tank is sparged[e] or used for heating or treating by means of an exothermic reaction, a fixed roof and a closed vent system shall be maintained that routes the organic HAP vapors to other process equipment or to a control device that meets the requirements of 40 CFR § 63.119(e)(1) or (e)(2).

[a] Where a tight fitting solid cover is required, it shall be maintained with no visible gaps or openings, except during periods of sampling, inspection, or maintenance.

[b] Manhole includes sumps and other points of access to a conveyance system.

[c] Applies to tanks with capacities of 38 m^3 or greater.

[d] A fixed roof may have openings necessary for proper venting of the tank, such as pressure/vacuum vent, j-pipe vent.

Table 36. COMPOUND LISTS USED FOR COMPLIANCE DEMONSTRATIONS FOR ENHANCED BIOLOGICAL TREATMENT PROCESSES (see § 63.145(b))

List 1	List 2	List 3
Acetonitrile	Acetaldehyde	Allyl Chloride
Acetophenone	Acrolein	Bromomethane
Acrylonitrile	Benzene	Butadiene 1,3
Biphenyl	Benzyl Chloride	Carbon Disulfide
Chlorobenzene	Bromoform	Carbon Tetrachloride
Dichloroethyl Ether	Cumene (isopropylbenzene)	Chloroethane (ethyl chloride)
Diethyl Sulfate	Dichlorobenzene 1,4	Chloroform
Dimethyl Sulfate	Dichloroethane 1,2	Chloroprene
Dimethyl Hydrazine 1,1	Dichloroethane 1,1 (ethylidenedichloride)	Dibromoethane 1,2
Dinitrophenol 2,4	Dichloropropane 1,2	Dichloroethene 1,1 (vinylidene chloride)
Dinitrotoluene 2,4	Dimethylaniline N,N	Dichloropropene 1,3
Dioxane 1,4	Epichlorohydrin	Hexane-n
Ethylene Glycol Monobutyl Ether Acetate	Ethyl Acrylate	Methyl Chloride
Ethylene Glycol Monomethyl Ether Acetate	Ethylbenzene	Methylene Chloride (dichloromethane)
Ethylene Glycol Dimethyl Ether	Ethylene Dibromide	Phosgene
Hexachlorobenzene	Ethylene Oxide	Propylene Oxide
Isophorone	Hexachlorobutadiene	Trichloroethane 1,12
Methanol	Hexachloroethane	Trichloroethylene
Methyl Methacrylate	Methyl Ethyl Ketone, (2 butanone)	Trimethylpentane 2,2,4

Table 36. COMPOUND LISTS USED FOR COMPLIANCE DEMONSTRATIONS FOR ENHANCED BIOLOGICAL TREATMENT PROCESSES (see § 63.145(b))

Nitrobenzene	Methyl Isobutyl Ketone	Vinyl Chloride
Toluidine	Methyl Tertiary Butyl Ether	
Trichlorobenzene 1,2,4	Naphathalene	
Trichlorophenol 2,4,6	Nitropropane 2	
Triethylamine	Propionaldehyde	
	Styrene	
	Tetrachloroethane 1,1,2,2	
	Toluene	
	Trichloroethane 1,1,1 (methyl chloroform)	
	Vinyl Acetate	
	Xylene-m	
	Xylene-o	
	Xylene-p	

Table 37. Default Biorates for List 1 Compounds

COMPOUND NAME	BIORATE, K1 L/g MLVSS-hr
ACETONITRILE	0.100
ACETOPHENONE	0.538
ACRYLONITRILE	0.750
BIPHENYL	5.643
CHLOROBENZENE	10.000
DICHLOROETHYL ETHER	0.246
DIETHYL SULFATE	0.105
DIMETHYL HYDRAZINE(1,1)	0.227
DIMETHYL SULFATE	0.178
DINITROPHENOL 2,4	0.620
DINITROTOLUENE(2,4)	0.784
DIOXANE(1,4)	0.393
ETHYLENE GLYCOL DIMETHYL ETHER	0.364
ETHYLENE GLYCOL MONOMETHYL ETHER ACETATE	0.159
ETHYLENE GLYCOL MONOBUTYL ETHER ACETATE	0.496
HEXACHLOROBENZENE	16.179
ISOPHORONE	0.598
METHANOL	0.200
METHYL METHACRYLATE	4.300
NITROBENZENE	2.300
TOLUIDINE (-0)	0.859
TRICHLOROBENZENE 1,2,4	4.393
TRICHLOROPHENOL 2,4,5	4.477
TRIETHYLAMINE	1.064

Figure 1. Definitions of Terms Used in Wastewater Equations

MAIN TERMS

AMR = Actual mass removal of Table 8 and/or Table 9 compounds achieved by treatment process or a series of treatment processes, kg/hr.

C = Concentration of Table 8 and/or Table 9 compounds in wastewater, ppmw.

CG = Concentration of TOC (minus methane and ethane) or total organic HAP, in vented gas stream, dry basis, ppmv.

CG_C = Concentration of TOC or organic HAP corrected to 3 percent oxygen, in vented gas stream, dry basis, ppmv.

CGS = Concentration of sample compounds in vented gas stream, dry basis, ppmv.

E = Removal or destruction efficiency, percent.

F_{bio} = Site-specific fraction of Table 8 or Table 9 compounds biodegraded, unitless.

Fm = Compound-specific fraction measured factor, unitless (listed in table 34).

Fr = Fraction removal value for Table 8 and/or Table 9 compounds, unitless (listed in Table 9).

Fr_{avg} = Flow-weighted average of the fraction removal (Fr) values.

i = Identifier for a compound.

j = Identifier for a sample.

k = Identifier for a run.

K_2 = Constant, $41.57 * 10^{-9}$, $(ppm)^{-1}$ (gram-mole per standard m^3)(kg/g), where standard temperature (gram-mole per standard m^3) is 20 ^oC.

m = Number of samples.

M = Mass, kg.

MW = Molecular weight, kg/kg-mole.

Figure 1. Definitions of Terms Used in Wastewater Equations

MAIN TERMS

n	=	Number of compounds.
p	=	Number of runs.
$\%O_{2d}$	=	Concentration of oxygen, dry basis, percent by volume
Q	=	Volumetric flowrate of wastewater, m^3/hr.
QG	=	Volumetric flow rate of vented gas stream, dry standard, m^3/min.
QMG	=	Mass flowrate of TOC (minus methane and ethane) or organic HAP, in vented gas stream, kg/hr.
QMW	=	Mass flowrate of Table 8 and/or Table 9 compounds in wastewater, kg/hr.
ρ	=	Density, kg/m^3.
RMR	=	Required mass removal achieved by treatment process or a series of treatment processes, kg/hr.
t_T	=	Total time of all runs, hr.

SUBSCRIPTS

a	=	Entering.
b	=	Exiting.
i	=	Identifier for a compound.
j	=	Identifier for a sample.
k	=	Identifier for a run.
m	=	Number of samples.
n	=	Number of compounds.
p	=	Number of runs.
T	=	Total; sum of individual.

51. Appendix A of Part 63 is amended by revising Methods 304A and 304B to read as follows:

Appendix A to Part 63-Test Methods

METHOD 304A: DETERMINATION OF BIODEGRADATION RATES OF ORGANIC COMPOUNDS (VENT OPTION)

1. Applicability and Principle

1.1 Applicability. This method is applicable for the determination of biodegradation rates of organic compounds in an activated sludge process. The test method is designed to evaluate the ability of an aerobic biological reaction system to degrade or destroy specific components in waste streams. The method may also be used to determine the effects of changes in wastewater composition on operation. The biodegradation rates determined by utilizing this method are not representative of a full-scale system. The rates measured by this method shall be used in conjunction with the procedures listed in Appendix C of this part to calculate the fraction emitted to the air versus the fraction biodegraded.

1.2 Principle. A self-contained benchtop bioreactor system is assembled in the laboratory. A sample of mixed liquor is added and the waste stream is then fed continuously. The benchtop bioreactor is operated under conditions nearly identical to the target full-scale activated sludge process. Bioreactor temperature, dissolved oxygen concentration, average residence time in the reactor, waste composition, biomass concentration, and biomass composition of the full-scale process are the

parameters which are duplicated in the benchtop bioreactor. Biomass shall be removed from the target full-scale activated sludge unit and held for no more than 4 hours prior to use in the benchtop bioreactor. If antifoaming agents are used in the full-scale system, they shall also be used in the benchtop bioreactor. The feed flowing into and the effluent exiting the benchtop bioreactor are analyzed to determine the biodegradation rates of the target compounds. The flow rate of the exit vent is used to calculate the concentration of target compounds (utilizing Henry's law) in the exit gas stream. If Henry's law constants for the compounds of interest are not known, this method cannot be used in the determination of the biodegradation rate and Method 304B is the suggested method. The choice of analytical methodology for measuring the compounds of interest at the inlet and outlet to the benchtop bioreactor are left to the discretion of the source, except where validated methods are available.

2. Apparatus

Figure 1 illustrates a typical laboratory apparatus used to measure biodegradation rates. While the following description refers to Figure 1, the EPA recognizes that alternative reactor configurations, such as alternative reactor shapes and locations of probes and the feed inlet, will also meet the intent of this method. Ensure that the benchtop bioreactor system is self-contained and isolated from the atmosphere (except for the exit vent stream) by leak-checking fittings, tubing, etc.

2.1 Laboratory apparatus.

2.1.1 Benchtop Bioreactor. The biological reaction is conducted in a biological oxidation reactor of at least 6 liters capacity . The benchtop bioreactor is sealed and equipped with internal probes for controlling and monitoring dissolved oxygen and internal temperature. The top of the reactor is equipped for aerators, gas flow ports, and

instrumentation (while ensuring that no leaks to the atmosphere exist around the fittings).

2.1.2 Aeration gas. Aeration gas is added to the benchtop bioreactor through three diffusers, which are glass tubes that extend to the bottom fifth of the reactor depth. A pure oxygen pressurized cylinder is recommended in order to maintain the specified oxygen concentration. Install a blower (e.g.,Diaphragm Type, 15 SCFH capacity) to blow the aeration gas into the reactor diffusers. Measure the aeration gas flow rate with a rotameter (e.g.,0-15 SCFH recommended). The aeration gas will rise through the benchtop bioreactor, dissolving oxygen into the mixture in the process. The aeration gas must provide sufficient agitation to keep the solids in suspension. Provide an exit for the aeration gas from the top flange of the benchtop bioreactor through a water-cooled (e.g., Allihn-type) vertical condenser. Install the condenser through a gas-tight fitting in the benchtop bioreactor closure. Install a splitter which directs a portion of the gas to an exit vent and the rest of the gas through an air recycle pump back to the benchtop bioreactor. Monitor and record the flow rate through the exit vent at least 3 times per day throughout the day.

2.1.3 Wastewater Feed. Supply the wastewater feed to the benchtop bioreactor in a collapsible low-density polyethylene container or collapsible liner in a container (e.g., 20 L) equipped with a spigot cap (collapsible containers or liners of other material may be required due to the permeability of some

volatile compounds through polyethylene). Obtain the wastewater feed by sampling the wastewater feed in the target process. A representative sample of wastewater shall be obtained from the piping leading to the aeration tank. This sample may be obtained from existing sampling valves at the discharge of the wastewater feed pump, or collected from a pipe discharging to the aeration tank, or by pumping from a well-mixed equalization tank upstream from the aeration tank. Alternatively, wastewater can be pumped continuously to the laboratory apparatus from a bleed stream taken from the equalization tank of the full-scale treatment system.

2.1.3.1 Refrigeration System. Keep the wastewater feed cool by ice or by refrigeration to 4 ^{O}C. If using a bleed stream from the equalization tank, refrigeration is not required if the residence time in the bleed stream is less than five minutes.

2.1.3.2 Wastewater Feed Pump. The wastewater is pumped from the refrigerated container using a variable-speed peristaltic pump drive equipped with a peristaltic pump head. Add the feed solution to the benchtop bioreactor through a fitting on the top flange. Determine the rate of feed addition to provide a retention time in the benchtop bioreactor that is numerically equivalent to the retention time in the full-scale system. The wastewater shall be fed at a rate sufficient to achieve 90 to 100 percent of the full-scale system residence time.

2.1.3.3 Treated wastewater feed. The benchtop bioreactor

effluent exits at the bottom of the reactor through a tube and proceeds to the clarifier.

2.1.4 Clarifier. The effluent flows to a separate closed clarifier that allows separation of biomass and effluent (e.g., 2-liter pear-shaped glass separatory funnel, modified by removing the stopcock and adding a 25-mm OD glass tube at the bottom). Benchtop bioreactor effluent enters the clarifier through a tube inserted to a depth of 0.08 m (3 in.) through a stopper at the top of the clarifier. System effluent flows from a tube inserted through the stopper at the top of the clarifier to a drain (or sample bottle when sampling). The underflow from the clarifier leaves from the glass tube at the bottom of the clarifier . Flexible tubing connects this fitting to the sludge recycle pump. This pump is coupled to a variable speed pump drive. The discharge from this pump is returned through a tube inserted in a port on the side of the benchtop bioreactor. An additional port is provided near the bottom of the benchtop bioreactor for sampling the reactor contents. The mixed liquor from the benchtop bioreactor flows into the center of the clarifier. The clarified system effluent separates from the biomass and flows through an exit near the top of the clarifier. There shall be no headspace in the clarifier.

2.1.5 Temperature Control Apparatus. Capable of maintaining the system at a temperature equal to the temperature of the full-scale system. The average temperature should be maintained within ±2 ^{O}C of the set point.

2.1.5.1 Temperature Monitoring Device. A resistance type temperature probe or a thermocouple connected to a temperature readout with a resolution of 0.1 ^{O}C or better.

2.1.5.2 Benchtop Bioreactor Heater. The heater is connected to the temperature control device.

2.1.6 Oxygen Control System. Maintain the dissolved oxygen concentration at the levels present in the full-scale system. Target full-scale activated sludge systems with dissolved oxygen concentration below 2 mg/L are required to maintain the dissolved oxygen concentration in the benchtop bioreactor at 0.5 mg/L of the target dissolved oxygen level. Target full-scale activated sludge systems with dissolved oxygen concentration above 2 mg/L are required to maintain the dissolved oxygen concentration in the benchtop bioreactor at 1.5 mg/L over the range of dissolved oxygen concentration. If the benchtop bioreactor is outside the control range, the dissolved oxygen is noted and the reactor operation is adjusted.

2.1.6.1 Dissolved Oxygen Monitor. Dissolved oxygen is monitored with a polarographic probe (gas permeable membrane) connected to a dissolved oxygen meter (e.g., 0 to 15 mg/L, 0 to 50 ^{O}C).

2.1.6.2 Benchtop bioreactor Pressure Monitor. The benchtop bioreactor pressure is monitored through a port in the top flange of the reactor. This is connected to a gauge control with a span of 13-cm water vacuum to 13-cm water pressure or better. A relay is activated when the vacuum exceeds an

adjustable setpoint which opens a solenoid valve (normally closed), admitting oxygen to the system. The vacuum setpoint controlling oxygen addition to the system shall be set at approximately 2.5 ± 0.5 cm water and maintained at this setting except during brief periods when the dissolved oxygen concentration is adjusted.

2.1.7 Connecting Tubing. All connecting tubing shall be Teflon or equivalent in impermeability. The only exception to this specification is the tubing directly inside the pump head of the wastewater feed pump, which may be Viton, Silicone or another type of flexible tubing. Note: Mention of trade names or products does not constitute endorsement by the U.S. Environmental Protection Agency.

2.2 Analysis. If the identity of the compounds of interest in the wastewater is not known , a representative sample of the wastewater shall be analyzed in order to identify all of the compounds of interest present. A gas chromatography/mass spectrometry screening method is recommended.

2.2.1 After identifying the compounds of interest in the wastewater, develop and/or use one or more analytical techniques capable of measuring each of those compounds (more than one analytical technique may be required, depending on the characteristics of the wastewater). Test Method 18, found in Appendix A of 40 CFR 60, may be used as a guideline in developing the analytical technique. Purge and trap techniques may be used for analysis providing the target components are sufficiently

volatile to make this technique appropriate. The limit of quantitation for each compound shall be determined[1]. If the effluent concentration of any target compound is below the limit of quantitation determined for that compound, the operation of the Method 304 unit may be altered to attempt to increase the effluent concentration above the limit of quantitation. Modifications to the method shall be approved prior to the test. The request should be addressed to Method 304 contact, Emissions Measurement Center, Mail Drop 19, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

2.2.2 Calibration Standards. Prepare calibration standards from pure certified standards in an aqueous medium. Prepare and analyze three concentrations of calibration standards for each target component (or for a mixture of components) in triplicate daily throughout the analyses of the test samples. At each concentration level, a single calibration shall be within 5 percent of the average of the three calibration results. The low and medium calibration standards shall bracket the expected concentration of the effluent (treated) wastewater. The medium and high standards shall bracket the expected influent concentration.

3. Reagents

3.1 Wastewater. Obtain a representative sample of wastewater at the inlet to the full-scale treatment plant if there is an existing full-scale treatment plant (See Section 2.1.3). If there is no existing full-scale treatment

plant, obtain the wastewater sample as close to the point of determination as possible. Collect the sample by pumping the wastewater into the 20-L collapsible container. The loss of volatiles shall be minimized from the wastewater by collapsing the container before filling, by minimizing the time of filling, and by avoiding a headspace in the container after filling. If the wastewater requires the addition of nutrients to support the biomass growth and maintain biomass characteristics, those nutrients are added and mixed with the container contents after the container is filled.

3.2 Biomass. Obtain the biomass or activated sludge used for rate constant determination in the bench-scale process from the existing full-scale process or from a representative biomass culture (e.g., biomass that has been developed for a future full-scale process). This biomass is preferentially obtained from a thickened acclimated mixed liquor sample. Collect the sample either by bailing from the mixed liquor in the aeration tank with a weighted container, or by collecting aeration tank effluent at the effluent overflow weir. Transport the sample to the laboratory within no more than 4 hours of collection. Maintain the biomass concentration in the benchtop bioreactor at the level of the full-scale system +10 percent throughout the sampling period of the test method.

4. Procedure. Safety Note: If explosive gases are produced as a byproduct of biodegradation and could realistically pose a hazard, closely monitor headspace concentration of these gases to

ensure laboratory safety. Placement of the benchtop bioreactor system inside a laboratory hood is recommended regardless of byproducts produced.

4.1 Benchtop bioreactor Operation. Charge the mixed liquor to the benchtop bioreactor, minimizing headspace over the liquid surface to minimize entrainment of mixed liquor in the circulating gas. Fasten the benchtop bioreactor headplate to the reactor over the liquid surface. Maintain the temperature of the contents of the benchtop bioreactor system at the temperature of the target full-scale system, +2 ^{O}C, throughout the testing period. Monitor and record the temperature of the benchtop bioreactor contents at least to the nearest 0.1 ^{O}C.

4.1.1 Wastewater Storage. Collect the wastewater sample in the 20-L collapsible container. Store the container at 4 ^{O}C throughout the testing period. Connect the container to the benchtop bioreactor feed pump.

4.1.2 Wastewater Flow Rate. The hydraulic residence time of the aeration tank is calculated as the ratio of the volume of the tank (L) to the flow rate (L/min). At the beginning of a test, the container shall be connected to the feed pump and solution shall be pumped to the benchtop bioreactor at the required flow rate to achieve the calculated hydraulic residence time of wastewater in the aeration tank.

$$Q_{test} = Q_{fs} \frac{L}{V_{fs}} \qquad \text{Eq. 304A-1}$$

where Q_{test} = wastewater flow rate (L/min)

Q_{fs} = average flow rate of full-scale process (L/min)

V_{fs} = volume of full-scale aeration tank (L)

The target flow rate in the test apparatus is the same as the flow rate in the target full-scale process multiplied by the ratio of benchtop bioreactor volume (e.g., 6 L) to the volume of the full-scale aeration tank. The hydraulic residence time shall be maintained at 90 to 100 percent of the residence time maintained in the full-scale unit. A nominal flow rate is set on the pump based on a pump calibration. Changes in the elasticity of the tubing in the pump head and the accumulation of material in the tubing affect this calibration. The nominal pumping rate shall be changed as necessary based on volumetric flow measurements. Discharge the benchtop bioreactor effluent to a wastewater storage, treatment, or disposal facility, except during sampling or flow measurement periods.

4.1.3 Sludge Recycle Rate. Set the sludge recycle rate at a rate sufficient to prevent accumulation in the bottom of the clarifier. Set the air circulation rate sufficient to maintain the biomass in suspension.

4.1.4 Benchtop Bioreactor Operation and Maintenance. Temperature, dissolved oxygen concentration, exit vent flow rate, benchtop bioreactor effluent flow rate, and air circulation rate shall be measured and recorded three times throughout each day of benchtop bioreactor operation. If other parameters (such as pH) are measured and maintained in the target full-scale unit, these

parameters, where appropriate, shall be monitored and maintained to target full-scale specifications in the benchtop bioreactor. At the beginning of each sampling period (Section 4.2), sample the benchtop bioreactor contents for suspended solids analysis. Take this sample by loosening a clamp on a length of tubing attached to the lower side port. Determine the suspended solids gravimetrically by the Gooch crucible/glass fiber filter method for total suspended solids, in accordance with Standard Methods[3] or equivalent. When necessary, sludge shall be wasted from the lower side port of the benchtop bioreactor, and the volume that is wasted shall be replaced with an equal volume of the reactor effluent. Add thickened activated sludge mixed liquor as necessary to the benchtop bioreactor to increase the suspended solids concentration to the desired level. Pump this mixed liquor to the benchtop bioreactor through the upper side port (Item 24 in Figure 1). Change the membrane on the dissolved oxygen probe before starting the test. Calibrate the oxygen probe immediately before the start of the test and each time the membrane is changed.

4.1.5 Inspection and Correction Procedures. If the feed line tubing becomes clogged, replace with new tubing. If the feed flow rate is not within 5 percent of target flow any time the flow rate is measured, reset pump or check the flow measuring device and measure flow rate again until target flow rate is achieved.

4.2 Test Sampling. At least two and one half hydraulic

residence times after the system has reached the targeted specifications shall be permitted to elapse before the first sample is taken. Effluent samples of the clarifier discharge (Item 20 in Figure 1) and the influent wastewater feed are collected in 40-mL septum vials to which two drops of 1:10 hydrochloric acid (HCl) in water have been added. Sample the clarifier discharge directly from the drain line. These samples will be composed of the entire flow from the system for a period of several minutes. Feed samples shall be taken from the feed pump suction line after temporarily stopping the benchtop bioreactor feed, removing a connector, and squeezing the collapsible feed container. Store both influent and effluent samples at 4 ^{O}C immediately after collection and analyze within 8 hours of collection.

4.2.1 Frequency of Sampling. During the test, sample and analyze the wastewater feed and the clarifier effluent at least six times. The sampling intervals shall be separated by at least 8 hours. During any individual sampling interval, sample the wastewater feed simultaneously with or immediately after the effluent sample. Calculate the relative standard deviation (RSD) of the amount removed (i.e., effluent concentration - wastewater feed concentration). The RSD values shall be < 15 percent. If an RSD value is > 15 percent, continue sampling and analyzing influent and effluent sets of samples until the RSD values are within specifications.

4.2.2 Sampling After Exposure of System to Atmosphere.

If, after starting sampling procedures, the benchtop bioreactor system is exposed to the atmosphere (due to leaks, maintenance, etc.), allow at least one hydraulic residence time to elapse before resuming sampling.

5. Operational Checks and Calibration

5.1 Dissolved Oxygen. Fluctuation in dissolved oxygen concentration may occur for numerous reasons, including undetected gas leaks, increases and decreases in mixed liquor suspended solids resulting from cell growth and solids loss in the effluent stream, changes in diffuser performance, cycling of effluent flow rate, and overcorrection due to faulty or sluggish dissolved oxygen probe response. Control the dissolved oxygen concentration in the benchtop bioreactor by changing the proportion of oxygen in the circulating aeration gas. Should the dissolved oxygen concentration drift below the designated experimental condition, bleed a small amount of aeration gas from the system on the pressure side (i. e. immediately upstream of one of the diffusers). This will create a vacuum in the system, triggering the pressure sensitive relay to open the solenoid valve and admit oxygen to the system. Should the dissolved oxygen concentration drift above the designated experimental condition, slow or stop the oxygen input to the system until the dissolved oxygen concentration approaches the correct level.

5.2 Sludge Wasting. Determine the suspended solids concentration (Section 4.1.4) at the beginning of a test, and once per day thereafter during the test. If the test is

completed within a two day period, determine the suspended solids concentration after the final sample set is taken. If the suspended solids concentration exceeds the specified concentration, remove a fraction of the sludge from the benchtop bioreactor. The required volume of mixed liquor to remove is determined as follows:

$$V_W = V_r \left(\frac{S_m - S_s}{S_m} \right) \qquad \text{Eq. 304A-2}$$

where V_W is the wasted volume (Liters),

V_r is the volume of the benchtop bioreactor (Liters),

S_m is the measured solids (g/L), and

S_S is the specified solids (g/L).

Remove the mixed liquor from the benchtop bioreactor by loosening a clamp on the mixed liquor sampling tube and allowing the required volume to drain to a graduated flask. Clamp the tube when the correct volume has been wasted. Replace the volume of the liquid wasted by pouring the same volume of effluent back into the benchtop bioreactor. Dispose of the waste sludge properly.

5.3 Sludge Makeup. In the event that the suspended solids concentration is lower than the specifications, add makeup sludge back into the benchtop bioreactor. Determine the amount of sludge added by the following equation:

$$V_W = V_r \left(\frac{S_s - S_m}{S_w} \right) \qquad \text{Eq. 304A-3}$$

where V_W is the volume of sludge to add (Liters),

V_r is the volume of the benchtop bioreactor (Liters),

S_W is the solids in the makeup sludge (g/L),

S_m is the measured solids (g/L), and

S_S is the specified solids (g/L).

5.4 Wastewater Pump Calibration. Determine the wastewater flow rate by collecting the system effluent for a time period of at least one hour, and measuring the volume with a graduated cylinder. Record the collection time period and volume collected. Determine flow rate. Adjust the pump speed to deliver the specified flow rate.

6. Calculations

6.1 Nomenclature. The following symbols are used in the calculations.

C_i = Average inlet feed concentration for a compound of interest, as analyzed (mg/L)

C_O = Average outlet (effluent) concentration for a compound of interest, as analyzed (mg/L)

X = Biomass concentration, mixed liquor suspended solids (g/L)

t = Hydraulic residence time in the benchtop bioreactor (hours)

V = Volume of the benchtop bioreactor (L)

Q = Flow rate of wastewater into the benchtop bioreactor, average (L/hour)

6.2 Residence Time. The hydraulic residence time of the benchtop bioreactor is equal to the ratio of the volume of the benchtop bioreactor (L) to the flow rate (L/h)

$$t = \frac{V}{Q} \qquad \text{Eq. 304A-4}$$

6.3 Rate of Biodegradation. Calculate the rate of biodegradation for each component with the following equation:

$$Rate\left(\frac{mg}{L\text{-}h}\right) = \frac{C_i - C_o}{t} \qquad \text{Eq. 304A-5}$$

6.4 First-Order Biorate Constant. Calculate the first-order biorate constant (K1) for each component with the following equation:

$$K1\left(\frac{L}{g\text{-}h}\right) = \frac{C_i - C_o}{t\ C_o\ X} \qquad \text{Eq. 304A-6}$$

6.5 Relative Standard Deviation (RSD). Determine the standard deviation of both the influent and effluent sample concentrations (S) using the following equation:

$$RSD = \frac{100}{\overline{S}}\left(\sum_{i=1}^{n}\frac{(S_i - \overline{S})^2}{(n-1)}\right)^{1/2} \qquad \text{Eq. 304A-7}$$

6.6 Determination of Percent Air Emissions and Percent Biodegraded. Use the results from this test method and follow the applicable procedures in Appendix C of 40 CFR Part 63, entitled, "Determination of the Fraction Biodegraded (F_{bio}) in a Biological Treatment Unit" to determine F_{bio}.

7. Bibliography

1. "Guidelines for data acquisition and data quality evaluation in Environmental Chemistry", Daniel MacDoughal, Analytical Chemistry, Volume 52, p. 2242, 1980.

2. Test Method 18, 40 CFR 60, Appendix A.

3. Standard Methods for the Examination of Water and Wastewater, 16th Edition, Method 209C, Total Suspended Solids Dried at 103-105 ^{O}C, APHA, 1985.

4. Water7, Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)- Air Emission Models, U.S. Environmental Protection Agency, EPA-450/3-87-026, Review Draft, November 1989.

5. Chemdat7, Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)- Air Emission Models, U.S. Environmental Protection Agency, EPA-450/3-87-026, Review Draft, November 1989.

METHOD 304B: DETERMINATION OF BIODEGRADATION RATES OF ORGANIC COMPOUNDS (SCRUBBER OPTION)

1. Applicability and Principle

1.1 Applicability. This method is applicable for the determination of biodegradation rates of organic compounds in an activated sludge process. The test method is designed to evaluate the ability of an aerobic biological reaction system to degrade or destroy specific components in waste streams. The method may also be used to determine the effects of changes in

wastewater composition on operation. The biodegradation rates determined by utilizing this method are not representative of a full-scale system. Full-scale systems embody biodegradation and air emissions in competing reactions. This method measures biodegradation in absence of air emissions. The rates measured by this method shall be used in conjunction with the procedures listed in Appendix C of this part to calculate the fraction emitted to the air versus the fraction biodegraded.

1.2 Principle. A self-contained benchtop bioreactor system is assembled in the laboratory. A sample of mixed liquor is added and the waste stream is then fed continuously. The benchtop bioreactor is operated under conditions nearly identical to the target full-scale activated sludge process, except that air emissions are not a factor. The benchtop bioreactor temperature, dissolved oxygen concentration, average residence time in the reactor, waste composition, biomass concentration, and biomass composition of the target full-scale process are the parameters which are duplicated in the laboratory system. Biomass shall be removed from the target full-scale activated sludge unit and held for no more than 4 hours prior to use in the benchtop bioreactor. If antifoaming agents are used in the full-scale system, they shall also be used in the benchtop bioreactor. The feed flowing into and the effluent exiting the benchtop bioreactor are analyzed to determine the biodegradation rates of the target compounds. The choice of analytical methodology for measuring the compounds of interest at the inlet and outlet to

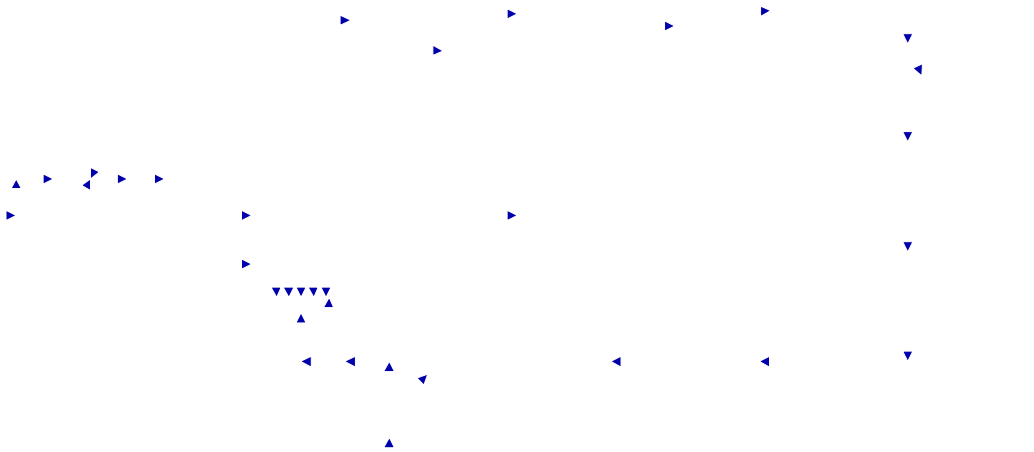
the benchtop bioreactor are left to the discretion of the source, except where validated methods are available.

2. Apparatus

Figure 1 illustrates a typical laboratory apparatus used to measure biodegradation rates. While the following description refers to Figure 1, the EPA recognizes that alternative reactor configurations, such as alternative reactor shapes and locations of probes and the feed inlet, will also meet the intent of this method. Ensure that the benchtop bioreactor system is self-contained and isolated from the atmosphere by leak-checking fittings, tubing, etc. 2.1 Laboratory apparatus.

2.1.1 Benchtop Bioreactor. The biological reaction is conducted in a biological oxidation reactor of at least 6-liters capacity . The benchtop bioreactor is sealed and equipped with internal probes for controlling and monitoring dissolved oxygen and internal temperature. The top of the benchtop bioreactor is equipped for aerators, gas flow ports, and instrumentation (while ensuring that no leaks to the atmosphere exist around the fittings).

2.1.2 Aeration gas. Aeration gas is added to the benchtop bioreactor through three diffusers, which are glass tubes that extend to the bottom fifth of the reactor depth. A pure oxygen pressurized cylinder is recommended in order to maintain the specified oxygen concentration. Install a blower (e.g., Diaphragm



Type, 15 SCFH capacity) to blow the aeration gas into the benchtop bioreactor diffusers. Measure the aeration gas flow rate with a rotameter (e.g., 0-15 SCFH recommended). The aeration gas will rise through the benchtop bioreactor, dissolving oxygen into the mixture in the process. The aeration gas must provide sufficient agitation to keep the solids in suspension. Provide an exit for the aeration gas from the top flange of the benchtop bioreactor through a water-cooled (e.g., Allihn-type) vertical condenser. Install the condenser through a gas-tight fitting in the benchtop bioreactor closure. Design the system so that at least 10 percent of the gas flows through an alkaline scrubber containing 175 mL of 45 percent by weight solution of potassium hydroxide (KOH) and 5 drops of 0.2 percent alizarin yellow dye. Route the balance of the gas through an adjustable scrubber bypass. Route all of the gas through a 1-L knock-out flask to remove entrained moisture and then to the intake of the blower. The blower recirculates the gas to the benchtop bioreactor.

2.1.3 Wastewater Feed. Supply the wastewater feed to the benchtop bioreactor in a collapsible low-density polyethylene container or collapsible liner in a container (e.g., 20 L) equipped with a spigot cap (collapsible containers or liners of other material may be required due to the permeability of some volatile compounds through polyethylene). Obtain the wastewater feed by sampling the wastewater feed in the target process. A representative sample of wastewater shall be obtained from the

piping leading to the aeration tank. This sample may be obtained from existing sampling valves at the discharge of the wastewater feed pump, or collected from a pipe discharging to the aeration tank, or by pumping from a well-mixed equalization tank upstream from the aeration tank. Alternatively, wastewater can be pumped continuously to the laboratory apparatus from a bleed stream taken from the equalization tank of the full-scale treatment system.

2.1.3.1 Refrigeration System. Keep the wastewater feed cool by ice or by refrigeration to 4°C. If using a bleed stream from the equalization tank, refrigeration is not required if the residence time in the bleed stream is less than five minutes.

2.1.3.2 Wastewater Feed Pump. The wastewater is pumped from the refrigerated container using a variable-speed peristaltic pump drive equipped with a peristaltic pump head. Add the feed solution to the benchtop bioreactor through a fitting on the top flange. Determine the rate of feed addition to provide a retention time in the benchtop bioreactor that is numerically equivalent to the retention time in the target full-scale system. The wastewater shall be fed at a rate sufficient to achieve 90 to 100 percent of the target full-scale system residence time.

2.1.3.3 Treated wastewater feed. The benchtop bioreactor effluent exits at the bottom of the reactor through a tube and proceeds to the clarifier.

2.1.4 Clarifier. The effluent flows to a separate closed clarifier that allows separation of biomass and effluent (e.g.,

2-liter pear-shaped glass separatory funnel, modified by removing the stopcock and adding a 25-mm OD glass tube at the bottom). Benchtop bioreactor effluent enters the clarifier through a tube inserted to a depth of 0.08 m (3 in.) through a stopper at the top of the clarifier. System effluent flows from a tube inserted through the stopper at the top of the clarifier to a drain (or sample bottle when sampling). The underflow from the clarifier leaves from the glass tube at the bottom of the clarifier . Flexible tubing connects this fitting to the sludge recycle pump. This pump is coupled to a variable speed pump drive. The discharge from this pump is returned through a tube inserted in a port on the side of the benchtop bioreactor. An additional port is provided near the bottom of the benchtop bioreactor for sampling the reactor contents. The mixed liquor from the benchtop bioreactor flows into the center of the clarifier. The clarified system effluent separates from the biomass and flows through an exit near the top of the clarifier. There shall be no headspace in the clarifier.

2.1.5 Temperature Control Apparatus. Capable of maintaining the system at a temperature equal to the temperature of the full-scale system. The average temperature should be maintained within ±2 ^{O}C of the set point.

2.1.5.1 Temperature Monitoring Device. A resistance type temperature probe or a thermocouple connected to a temperature readout with a resolution of 0.1°C or better.

2.1.5.2 Benchtop Bioreactor Heater. The heater is connected

to the temperature control device.

2.1.6 Oxygen Control System. Maintain the dissolved oxygen concentration at the levels present in the full-scale system. Target full-scale activated sludge systems with dissolved oxygen concentration below 2 mg/L are required to maintain the dissolved oxygen concentration in the benchtop bioreactor at 0.5 mg/L of the target dissolved oxygen level. Target full-scale activated sludge systems with dissolved oxygen concentration above 2 mg/L are required to maintain the dissolved oxygen concentration in the benchtop bioreactor at 1.5 mg/L over the range of dissolved oxygen concentration. If the benchtop bioreactor is outside the control range, the dissolved oxygen is noted and the reactor operation is adjusted.

2.1.6.1 Dissolved Oxygen Monitor. Dissolved oxygen is monitored with a polarographic probe (gas permeable membrane) connected to a dissolved oxygen meter (e.g., 0 to 15 mg/L, 0 to 50°C).

2.1.6.2 Benchtop Bioreactor Pressure Monitor. The benchtop bioreactor pressure is monitored through a port in the top flange of the reactor. This is connected to a gauge control with a span of 13-cm water vacuum to 13-cm water pressure or better. A relay is activated when the vacuum exceeds an adjustable setpoint which opens a solenoid valve (normally closed), admitting oxygen to the system. The vacuum setpoint controlling oxygen addition to the system shall be set at approximately 2.5 ± 0.5 cm water and maintained at this setting except during brief periods when the

dissolved oxygen concentration is adjusted.

2.1.7 Connecting Tubing. All connecting tubing shall be Teflon or equivalent in impermeability. The only exception to this specification is the tubing directly inside the pump head of the wastewater feed pump, which may be Viton, Silicone or another type of flexible tubing. Note: Mention of trade names or products does not constitute endorsement by the U.S. Environmental Protection Agency.

2.2 Analysis. If the identity of the compounds of interest in the wastewater is not known , a representative sample of the wastewater shall be analyzed in order to identify all of the compounds of interest present. A gas chromatography/mass spectrometry screening method is recommended.

2.2.1 After identifying the compounds of interest in the wastewater, develop and/or use one or more analytical technique capable of measuring each of those compounds (more than one analytical technique may be required, depending on the characteristics of the wastewater). Method 18, found in Appendix A of 40 CFR 60, may be used as a guideline in developing the analytical technique. Purge and trap techniques may be used for analysis providing the target components are sufficiently volatile to make this technique appropriate. The limit of quantitation for each compound shall be determined[1]. If the effluent concentration of any target compound is below the limit of quantitation determined for that compound, the operation of the Method 304 unit may be altered to attempt to increase the

effluent concentration above the limit of quantitation. Modifications to the method shall be approved prior to the test. The request should be addressed to Method 304 contact, Emissions Measurement Center, Mail Drop 19, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

2.2.2 Calibration Standards. Prepare calibration standards from pure certified standards in an aqueous medium. Prepare and analyze three concentrations of calibration standards for each target component (or for a mixture of components) in triplicate daily throughout the analyses of the test samples. At each concentration level, a single calibration shall be within 5 percent of the average of the three calibration results. The low and medium calibration standards shall bracket the expected concentration of the effluent (treated) wastewater. The medium and high standards shall bracket the expected influent concentration.

3. Reagents

3.1 Wastewater. Obtain a representative sample of wastewater at the inlet to the full-scale treatment plant if there is an existing full-scale treatment plant (See Section 2.1.3). If there is no existing full-scale treatment plant, obtain the wastewater sample as close to the point of determination as possible. Collect the sample by pumping the wastewater into the 20-L collapsible container. The loss of volatiles shall be minimized from the wastewater by collapsing the container before filling, by minimizing the time of filling,

and by avoiding a headspace in the container after filling. If the wastewater requires the addition of nutrients to support the biomass growth and maintain biomass characteristics, those nutrients are added and mixed with the container contents after the container is filled.

3.2 Biomass. Obtain the biomass or activated sludge used for rate constant determination in the bench-scale process from the existing full-scale process or from a representative biomass culture (e.g., biomass that has been developed for a future full-scale process). This biomass is preferentially obtained from a thickened acclimated mixed liquor sample. Collect the sample either by bailing from the mixed liquor in the aeration tank with a weighted container, or by collecting aeration tank effluent at the effluent overflow weir. Transport the sample to the laboratory within no more than 4 hours of collection. Maintain the biomass concentration in the benchtop bioreactor at the level of the target full-scale system +10 percent throughout the sampling period of the test method.

4. Procedure. Safety Note: If explosive gases are produced as a byproduct of biodegradation and could realistically pose a hazard, closely monitor headspace concentration of these gases to ensure laboratory safety. Placement of the benchtop bioreactor system inside a laboratory hood is recommended regardless of byproducts produced.

4.1 Benchtop Bioreactor Operation. Charge the mixed liquor to the benchtop bioreactor, minimizing headspace over the liquid

surface to minimize entrainment of mixed liquor in the circulating gas. Fasten the benchtop bioreactor headplate to the reactor over the liquid surface. Maintain the temperature of the contents of the benchtop bioreactor system at the temperature of the target full-scale system, +2°C, throughout the testing period. Monitor and record the temperature of the reactor contents at least to the nearest 0.1°C.

4.1.1 Wastewater Storage. Collect the wastewater sample in the 20-L collapsible container. Store the container at 4°C throughout the testing period. Connect the container to the benchtop bioreactor feed pump.

4.1.2 Wastewater Flow Rate. The hydraulic residence time of the aeration tank is calculated as the ratio of the volume of the tank (L) to the flow rate (L/min). At the beginning of a test, the container shall be connected to the feed pump and solution shall be pumped to the benchtop bioreactor at the required flow rate to achieve the calculated hydraulic residence time of wastewater in the aeration tank.

$$Q_{test} = Q_{fs} \frac{L}{V_{fs}} \qquad \text{Eq. 304B-1}$$

where Q_{test} = wastewater flow rate (L/min)

Q_{fs} = average flow rate of full-scale process (L/min)

V_{fs} = volume of full-scale aeration tank (L)

The target flow rate in the test apparatus is the same as the flow rate in the target full-scale process multiplied by the

ratio of benchtop bioreactor volume (e.g., 6 L) to the volume of the full-scale aeration tank. The hydraulic residence time shall be maintained at 90 to 100 percent of the residence time maintained in the target full-scale unit. A nominal flow rate is set on the pump based on a pump calibration. Changes in the elasticity of the tubing in the pump head and the accumulation of material in the tubing affect this calibration. The nominal pumping rate shall be changed as necessary based on volumetric flow measurements. Discharge the benchtop bioreactor effluent to a wastewater storage, treatment, or disposal facility, except during sampling or flow measurement periods.

4.1.3 Sludge Recycle Rate. Set the sludge recycle rate at a rate sufficient to prevent accumulation in the bottom of the clarifier. Set the air circulation rate sufficient to maintain the biomass in suspension.

4.1.4 Benchtop Bioreactor Operation and Maintenance. Temperature, dissolved oxygen concentration, flow rate, and air circulation rate shall be measured and recorded three times throughout each day of testing. If other parameters (such as pH) are measured and maintained in the target full-scale unit, these parameters shall, where appropriate, be monitored and maintained to full-scale specifications in the benchtop bioreactor. At the beginning of each sampling period (Section 4.2), sample the benchtop bioreactor contents for suspended solids analysis. Take this sample by loosening a clamp on a length of tubing attached to the lower side port. Determine the suspended solids

gravimetrically by the Gooch crucible/glass fiber filter method for total suspended solids, in accordance with Standard Methods[3] or equivalent. When necessary, sludge shall be wasted from the lower side port of the benchtop bioreactor, and the volume that is wasted shall be replaced with an equal volume of the benchtop bioreactor effluent. Add thickened activated sludge mixed liquor as necessary to the benchtop bioreactor to increase the suspended solids concentration to the desired level. Pump this mixed liquor to the benchtop bioreactor through the upper side port (Item 24 in Figure 1). Change the membrane on the dissolved oxygen probe before starting the test. Calibrate the oxygen probe immediately before the start of the test and each time the membrane is changed. The scrubber solution shall be replaced each weekday with 175 mL 45 percent W/W KOH solution to which five drops of 0.2 percent alizarin yellow indicator in water have been added. The potassium hydroxide solution in the alkaline scrubber shall be changed if the alizarin yellow dye color changes.

4.1.5 Inspection and Correction Procedures. If the feed line tubing becomes clogged, replace with new tubing. If the feed flow rate is not within 5 percent of target flow any time the flow rate is measured, reset pump or check the flow measuring device and measure flow rate again until target flow rate is achieved.

4.2 Test Sampling. At least two and one half hydraulic residence times after the system has reached the targeted

specifications shall be permitted to elapse before the first sample is taken. Effluent samples of the clarifier discharge (Item 20 in Figure 1) and the influent wastewater feed are collected in 40-mL septum vials to which two drops of 1:10 hydrochloric acid (HCl) in water have been added. Sample the clarifier discharge directly from the drain line. These samples will be composed of the entire flow from the system for a period of several minutes. Feed samples shall be taken from the feed pump suction line after temporarily stopping the benchtop bioreactor feed, removing a connector, and squeezing the collapsible feed container. Store both influent and effluent samples at 4°C immediately after collection and analyze within 8 hours of collection.

4.2.1 Frequency of Sampling. During the test, sample and analyze the wastewater feed and the clarifier effluent at least six times. The sampling intervals shall be separated by at least 8 hours. During any individual sampling interval, sample the wastewater feed simultaneously with or immediately after the effluent sample. Calculate the relative standard deviation (RSD) of the amount removed (i.e., effluent concentration - wastewater feed concentration) . The RSD values shall be < 15 percent. If an RSD value is > 15 percent, continue sampling and analyzing influent and effluent sets of samples until the RSD values are within specifications.

4.2.2 Sampling After Exposure of System to Atmosphere. If, after starting sampling procedures, the benchtop bioreactor

system is exposed to the atmosphere (due to leaks, maintenance, etc.), allow at least one hydraulic residence time to elapse before resuming sampling.

5. Operational Checks and Calibration

5.1 Dissolved Oxygen. Fluctuation in dissolved oxygen concentration may occur for numerous reasons, including undetected gas leaks, increases and decreases in mixed liquor suspended solids resulting from cell growth and solids loss in the effluent stream, changes in diffuser performance, cycling of effluent flow rate, and overcorrection due to faulty or sluggish dissolved oxygen probe response. Control the dissolved oxygen concentration in the benchtop bioreactor by changing the proportion of oxygen in the circulating aeration gas. Should the dissolved oxygen concentration drift below the designated experimental condition, bleed a small amount of aeration gas from the system on the pressure side (i. e. immediately upstream of one of the diffusers). This will create a vacuum in the system, triggering the pressure sensitive relay to open the solenoid valve and admit oxygen to the system. Should the dissolved oxygen concentration drift above the designated experimental condition, slow or stop the oxygen input to the system until the dissolved oxygen concentration approaches the correct level.

5.2 Sludge Wasting. Determine the suspended solids concentration (Section 4.1.4) at the beginning of a test, and once per day thereafter during the test. If the test is completed within a two day period, determine the suspended solids

concentration after the final sample set is taken. If the suspended solids concentration exceeds the specified concentration, remove a fraction of the sludge from the benchtop bioreactor. The required volume of mixed liquor to remove is determined as follows:

$$V_w = V_r \left(\frac{S_m - S_s}{S_m} \right) \qquad \text{Eq. 304B-2}$$

where V_W is the wasted volume (Liters),

V_r is the volume of the benchtop bioreactor (Liters),

S_m is the measured solids (g/L), and

S_S is the specified solids (g/L).

Remove the mixed liquor from the benchtop bioreactor by loosening a clamp on the mixed liquor sampling tube and allowing the required volume to drain to a graduated flask. Clamp the tube when the correct volume has been wasted. Replace the volume of the liquid wasted by pouring the same volume of effluent back into the benchtop bioreactor. Dispose of the waste sludge properly.

5.3 Sludge Makeup. In the event that the suspended solids concentration is lower than the specifications, add makeup sludge back into the benchtop bioreactor. Determine the amount of sludge added by the following equation:

$$V_w = V_r \left(\frac{S_s - S_m}{S_w} \right) \qquad \text{Eq. 304B-3}$$

where V_w is the volume of sludge to add (Liters),

V_r is the volume of the benchtop bioreactor (Liters),

S_w is the solids in the makeup sludge (g/L),

S_m is the measured solids (g/L), and

S_s is the specified solids (g/L).

5.4 Wastewater Pump Calibration. Determine the wastewater flow rate by collecting the system effluent for a time period of at least one hour, and measuring the volume with a graduated cylinder. Record the collection time period and volume collected. Determine flow rate. Adjust the pump speed to deliver the specified flow rate.

6. Calculations

6.1 Nomenclature. The following symbols are used in the calculations.

C_i = Average inlet feed concentration for a compound of interest, as analyzed (mg/L)

C_o = Average outlet (effluent) concentration for a compound of interest, as analyzed (mg/L)

X = Biomass concentration, mixed liquor suspended solids (g/L)

t = Hydraulic residence time in the benchtop bioreactor (hours)

V = Volume of the benchtop bioreactor (L)

Q = Flow rate of wastewater into the benchtop bioreactor, average (L/hour)

6.2 Residence Time. The hydraulic residence time of the benchtop bioreactor is equal to the ratio of the volume of the benchtop bioreactor (L) to the flow rate (L/h)

$$t = \frac{V}{Q} \qquad \text{Eq. 304B-4}$$

6.3 Rate of Biodegradation. Calculate the rate of biodegradation for each component with the following equation:

$$Rate\ \left(\frac{mg}{L\text{-}h}\right) = \frac{C_i - C_o}{t} \qquad \text{Eq. 304B-5}$$

6.4 First-Order Biorate Constant. Calculate the first-order biorate constant (K1) for each component with the following equation:

$$K1\left(\frac{L}{g\text{-}h}\right) = \frac{C_i - C_o}{t\ C_o\ X} \qquad \text{Eq. 304B-6}$$

6.5 Relative Standard Deviation (RSD). Determine the standard deviation of both the influent and effluent sample concentrations (S) using the following equation:

$$RSD = \frac{100}{\overline{S}} \left(\sum_{i=1}^{n} \frac{(S_i - \overline{S})^2}{(n-1)} \right)^{1/2} \qquad \text{Eq. 304B-7}$$

6.6 Determination of Percent Air Emissions and Percent Biodegraded. Use the results from this test method and follow the applicable procedures in Appendix C of 40 CFR Part 63, entitled, "Determination of the Fraction Biodegraded (F_{bio}) in a

Biological Treatment Unit" to determine F_{bio}.

7. Bibliography

1. "Guidelines for data acquisition and data quality evaluation in Environmental Chemistry", Daniel MacDoughal, **Analytical Chemistry**, Volume 52, p. 2242, 1980.
2. Test Method 18, 40 CFR 60, Appendix A.
3. Standard Methods for the Examination of Water and Wastewater, 16^{th} Edition, Method 209C, Total Suspended Solids Dried at 103-105°C, APHA, 1985.
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5. Chemdat7, Hazardous Waste Treatment, Storage, and disposal Facilities (TSDF)- Air Emission Models, U.S. Environmental Protection Agency, EPA-450/3-87-026, Review Draft, November 1989.

52. Appendix C of Part 63 is revised to read as follows:

Appendix C to part 63

Determination of the Fraction Biodegraded (F_{bio}) in a Biological Treatment Unit

I. Purpose

The purpose of this appendix is to define the procedures for an owner or operator to use to calculate the site specific fraction of organic compounds biodegraded (F_{bio}) in a biological treatment unit. If an acceptable level of organic compounds is

destroyed rather than emitted to the air or remaining in the effluent, the biological treatment unit may be used to comply with the applicable treatment requirements without the unit being covered and vented through a closed vent system to an air pollution control device.

The determination of F_{bio} shall be made on a system as it would exist under the rule. The owner or operator should anticipate changes that would occur to the wastewater flow and concentration of organics, to be treated by the biological treatment unit, as a result of enclosing the collection and treatment system as required by the rule.

II. Definitions

Biological treatment unit = wastewater treatment unit designed and operated to promote the growth of bacteria to destroy organic materials in wastewater.

f_{bio} = The fraction of individual applicable organic compounds in the wastewater biodegraded in a biological treatment unit.

F_{bio} = The fraction of total applicable organic compounds in the wastewater biodegraded in a biological treatment unit.

Fe = The fraction of applicable organic compounds emitted from the wastewater to the atmosphere.

K1 = First order biodegradation rate constant, L/g MLVSS-hr

KL = liquid-phase mass transfer coefficient, m/s

M = compound specific mass flow weighted average of organic compounds in the wastewater, Mg/Yr

III. Procedures for Determination of f_{bio}

The first step in the analysis to determine if a biological treatment unit may be used without being covered and vented through a closed-vent system to an air pollution control device, is to determine the compound-specific f_{bio}. The following four procedures may be used to determine f_{bio}:

1) EPA Test Method 304A or 304B (Appendix A, Part 63) - Method for the Determination of Biodegradation Rates of Organic Compounds,
2) Performance data with and without biodegradation,
3) Inlet and outlet concentration measurements,
4) Batch Tests.

All procedures must be executed so that the resulting F_{bio} is based on the collection system and waste management units being in compliance with the regulation. If the collection system and waste management units meet the suppression requirements at the time of the test, any of the four procedures may be chosen. If the collection system and waste management units are not in compliance at the time of the performance test, then only Method 304A, 304B, or the Batch Test shall be chosen. If Method 304A, 304B, or the Batch Test is used, any anticipated changes to the influent of the full-scale biological treatment unit that will occur after the facility has enclosed the collection system must be represented in the influent feed to the benchtop bioreactor unit, or test unit.

Select one or more appropriate procedures from the four listed above based on the availability of site specific data. If

the facility does not have site-specific data on the removal efficiency of its biological treatment unit, then Procedure 1 or Procedure 4 may be used. Procedure 1 allows the use of a benchtop bioreactor to determine the first-order biodegradation rate constant. For compounds that represent a small proportion of the mass of the regulated compounds in the wastewater, an owner or operator may elect to assume the first order biodegradation constant is zero. Procedure 4 explains two types of batch tests which may be used to estimate the first order biodegradation rate constant. For compounds that represent a small proportion of the mass of the regulated compounds in the wastewater, an owner or operator may elect to assume the first order biodegradation constant is zero. Procedure 3 would be used if the facility has, or measures to determine, data on the inlet and outlet individual organic compound concentration for the biological treatment unit. Procedure 2 is used if a facility has or obtains performance data on a biotreatment unit prior to and after addition of the microbial mass. An example where Procedure 2 could be used, is an activated sludge unit where measurements have been taken on inlet and exit concentration of organic compounds in the wastewater prior to seeding with the microbial mass and start-up of the unit. The flow chart in Figure 1 outlines the steps to use for each of the procedures.

A. Method 304A or 304B (Procedure 1)

If the first procedure is selected, follow the instructions in Appendix A of Part 63 Method 304A "Method for the

Determination of Biodegradation Rates of Organic Compounds (Vented Option)" or Method 304B "Method for the Determination of Biodegradation Rates of Organic Compounds (Scrubber Option)". Method 304A or 304B provides instruction on setting up and operating a self-contained benchtop bioreactor system which is operated under conditions representative of the target full-scale system. Method 304A uses a benchtop bioreactor system with a vent, and uses modeling to estimate any air emissions. Method 304B uses a benchtop bioreactor system which is equipped with a scrubber and is not vented.

There are some restrictions on which method a source may use. If the facility is measuring the rate of biodegradation of compounds that may tend to react or hydrolyze in the scrubber of Method 304B, this method shall not be used and Method 304A is the required method. If a Henry’s law value is not available to use with Form V, then Method 304A shall not be used and Method 304B is the required method. When using either method, the feed flow to the benchtop bioreactor shall be representative of the flow and concentration of the wastewater that will be treated by the full-scale biological treatment unit after the collection and treatment system has been enclosed as required under the applicable subpart.

The conditions under which the full-scale biological treatment unit is run establishes the operating parameters of Method 304A or 304B. If the biological treatment unit is operated under abnormal operating conditions (conditions outside

the range of critical parameters examined and confirmed in the laboratory), the Agency believes this will adversely affect the biodegradation rate and is an unacceptable treatment option. The facility would be making multiple runs of the test method to simulate the operating range for its biological treatment unit. For wide ranges of variation in operating parameters, the facility shall demonstrate the biological treatment unit is achieving an acceptable level of control, as required by the regulation, across the ranges and not only at the endpoints.

If Method 304A is used, complete Form V initially. Form V is used to calculate K1 from the Method 304A results. Form V uses the Henry's law constant to estimate the fraction lost from the benchtop reactor vent. The owner or operator shall use the Henry's law values in Table I. Form V also gives direction for calculating an equivalent KL. Note on Form V if the calculated number for line 11 is greater than the calculated value for line 13, this procedure shall not be used to demonstrate the compound is biodegradable. If line 11 is greater than line 13, this is an indication the fraction emitted from the vent is greater than the fraction biodegraded. The equivalent KL determined on Form V is used in Form II (line 6). Estimation of the Fe and f_{bio} must be done following the steps in Form III. Form III uses the previously calculated values of K1 and KL (equivalent KL), and site-specific parameters of the full-scale bioreactor as input to the calculations. Forms II, III, and V must be completed for each organic compound in the wastewater to determine Fe and f_{bio}.

If Method 304B is used, perform the method and use the measurements to determine K1, which is the first-order biodegradation rate constant. Form I lists the sequence of steps in the procedure for calculating K1 from the Method 304B results. Once K1 is determined, KL must be calculated by use of mass transfer equations. Form II outlines the procedure to follow for use of mass transfer equations to determine KL. A computer program which incorporates these mass transfer equations may be used. Water7 is a program that incorporates these mass transfer equations and may be used to determine KL. Refer to Form II-A to determine KL, if Water7 or the most recent update to this model is used. In addition, the Bay Area Sewage Toxics Emission (BASTE) model version 3.0 or equivalent upgrade and the TOXCHEM (Environment Canada's Wastewater Technology Centre and Environmega, Ltd.) model version 1.10 or equivalent upgrade may also be used to determine KL for the biological treatment unit with several stipulations. The programs must be altered to output a KL value which is based on the site-specific parameters of the unit modeled, and the Henry's law values listed in table I must be substituted for the existing Henry's law values in the programs. Input values used in the model and corresponding output values shall become documentation of the f_{bio} determination. The owner or operator should be aware these programs do not allow modeling of certain units. To model these units, the owner or operator shall use one of the other appropriate procedures as outlined in this appendix. The owner

or operator shall not use a default value for KL. The KL value determined by use of these models shall be based on the site-specific parameters of the specific unit. This KL value shall be inserted in Form II (line 6). Estimation of the Fe and f_{bio} must be done following the steps in Form III. Form III uses the previously calculated values of K1 and KL, and site-specific parameters of the full-scale bioreactor as input to the calculations. Forms I, II, and III must be completed for each organic compound in the wastewater to determine Fe and f_{bio}.

B. Performance Data With and Without Biodegradation (Procedure 2)

Procedure 2 uses site-specific performance data that represents or characterizes operation of the unit both with and without biodegradation. As previously mentioned, proper determination of f_{bio} must be made on a system as it would exist under the rule. Using Form IV, calculate KL and K1. After KL and K1 are determined, Form III is used to calculate Fe and f_{bio} for each organic compound present in the wastewater.

C. Inlet and Outlet Concentration Measurements (Procedure 3)

Procedure 3 uses measured inlet and outlet organic compound concentrations for the unit. Again, proper determination of f_{bio} must be made on a system as it would exist under the rule. The first step in using this procedure is to calculate KL using Form II. A computer model may be used. If the Water7 model or the most recent update to this model is used, then use Form II-A to

calculate KL. After KL is determined using field data, complete Form VI to calculate K1. The TOXCHEM or BASTE model may also be used to calculate KL for the biological treatment unit, with the stipulations listed in procedure 304B. After KL and K1 are determined, Form III is used to calculate Fe and f_{bio} for each organic compound.

D. Batch Tests (Procedure 4)

Two types of batch tests which may be used to determine kinetic parameters are: (1) the aerated reactor test and (2) the sealed reactor test. The aerated reactor test is also known as the BOX test (batch test with oxygen addition). The sealed reactor test is also known as the serum bottle test. These batch tests should be conducted only by persons familiar with procedures for determining biodegradation kinetics. Detailed discussions of batch procedures for determining biodegradation kinetic parameters can be found in references 1 - 4.

For both batch test approaches, a biomass sample from the activated sludge unit of interest is collected, aerated, and stored for no more than 4 hours prior to testing. To collect sufficient data when biodegradation is rapid, it may be necessary to dilute the biomass sample. If the sample is to be diluted, the biomass sample shall be diluted using treated effluent from the activated sludge unit of interest to a concentration such that the biodegradation test will last long enough to make at least six concentration measurements. It is recommended that the tests not be terminated until the compound concentration falls

below the limit of quantitation (LOQ). Measurements that are below the LOQ should not be used in the data analysis. Biomass concentrations shall be determined using standard methods for measurement of mixed liquor volatile suspended solids (MLVSS) (reference 5).

The change in concentration of a test compound may be monitored by either measuring the concentration in the liquid or in the reactor headspace. The analytical technique chosen for the test should be as sensitive as possible. For the batch test procedures described in this section, equilibrium conditions must exist between the liquid and gas phases of the experiments because the data analysis procedures are based on this premise. To use the headspace sampling approach, the reactor headspace must be in equilibrium with the liquid so that the headspace concentrations can be correlated with the liquid concentrations. Before the biodegradation testing is conducted, the equilibrium assumption must be verified. A discussion of the equilibrium assumption verification is given below in sections D.1 and D.2 since different approaches are required for the two types of batch tests.

To determine biodegradation kinetic parameters in a batch test, it is important to choose an appropriate initial substrate (compound(s) of interest) concentration for the test. The outcome of the batch experiment may be influenced by the initial substrate (So) to biomass (X_o) ratio (see references 3, 4, and 6)). This ratio is typically measured in chemical oxygen demand

(COD) units. When the S_o/X_o ratio is low, cell multiplication and growth in the batch test is negligible and the kinetics measured by the test are representative of the kinetics in the activated sludge unit of interest. The S_o/X_o ratio for a batch test is determined with the following equation:

$$\frac{S_o}{X_o} = \frac{S_i}{1.42\ X} \qquad \text{(Eqn App. C-1)}$$

where:

S_o/X_o = initial substrate to biomass ratio on a COD basis

S_i = initial substrate concentration in COD units (g COD/L)

X = biomass concentration in the batch test (g MLVSS/L)

1.42 = Conversion factor to convert to COD units

For the batch tests described in this section, the S_o/X_o ratio (on a COD basis) must be initially less than 0.5.

1. Aerated Reactor Test. An aerated draft tube reactor may be used for the biokinetics testing (as an example see Figure 2 of Appendix C). Other aerated reactor configurations may also be used. Air is bubbled through a porous frit at a rate sufficient to aerate and keep the reactor uniformly mixed. Aeration rates typically vary from 50 to 200 ml/min for a 1 liter system. A mass flow rate controller is used to carefully control

the air flow rate because it is important to have an accurate measure of this rate. The dissolved oxygen (DO) concentration in the system must not fall below 2 mg/liter so that the biodegradation observed will not be DO-limited. Once the air flow rate is established, the test mixture (or compound) of interest is then injected into the reactor and the concentration of the compound(s) is monitored over time. Concentrations may be monitored in the liquid or in the headspace. A minimum of six samples shall be taken over the period of the test. However, it is necessary to collect samples until the compound concentration falls below the LOQ. If liquid samples are collected, they must be small enough such that the liquid volume in the batch reactor does not change by more than 10%.

Before conducting experiments with biomass, it is necessary to verify the equilibrium assumption. The equilibrium assumption can be verified by conducting a stripping experiment using the effluent (no biomass) from the activated sludge unit of interest. Effluent is filtered with a 0.45 um or smaller filter and placed in the draft tube reactor. Air is sparged into the system and the compound concentration in the liquid or headspace is monitored over time. This test with no biomass may provide an estimate of the Henry's law constant. If the system is at equilibrium, the Henry's law constant may be estimated with the following equation:

$$- \ln(C/C_O)=(GK_{eq}/V)t \qquad \text{(Eqn App. C-2)}$$

where:

C = concentration at time, t (min)

C_o = concentration at t = 0

G = volumetric gas flow rate (ml/min)

V = liquid volume in the batch reactor (ml)

K_{eq} = Henry's law constant(mg/L-gas)/(mg/L-liquid)

t = time (min)

A plot of $-\ln(C/C_o)$ as a function of t will have a slope equal to GK_{eq}/V. The equilibrium assumption can be verified by comparing the experimentally determined K_{eq} for the system to literature values of the Henry's Law constant (including those listed in this appendix). If K_{eq} does not match the Henry's law constant, K_{eq} shall be determined from analysis of the headspace and liquid concentration in a batch system.

The concentration of a compound decreases in the bioreactor due to both biodegradation and stripping. Biodegradation processes are typically described with a Monod model. This model and a stripping expression are combined to give a mass balance for the aerated draft tube reactor):

$$-\frac{ds}{dt} = \left(\frac{GK_{eq}}{V}\right)s + \left(\frac{Q_m X}{K_s + s}\right)s \qquad \text{(Eqn App. C-3)}$$

where:

s = test compound concentration, mg/liter

G = volumetric gas flow rate, liters/hr

K_{eq} = Henry's Law constant measured in the system, (mg/liter gas)/(mg/liter liquid)

V = volume of liquid in the reactor, liters

X = biomass concentration (g MLVSS/liter)

Q_m = maximum rate of substrate removal, mg/g MLVSS/hr

K_S = Monod biorate constant at half the maximum rate, mg/liter

Equation App.C-3 has the analytical solution:

$$-t=\frac{VK_s}{A}\ln\left(\frac{s}{s_0}\right)+\frac{Q_m X V^2}{AB}\ln\left(\frac{A+Bs}{A+Bs_0}\right) \qquad \text{(Eqn App. C-4)}$$

where:

A = $GK_{eq}K_S + Q_mVX$

B = GK_{eq}

s_o = test compound concentration at t=0

This equation is used along with the substrate concentration versus time data to determine the best fit parameters (Q_m and K_S) to describe the biodegradation process in the aerated reactor. If the Aerated Reactor test is used, the following procedure is used to analyze the data. Evaluate K_{eq} for the compound of interest with Form XI. The concentration in the vented headspace or liquid is measured as a function of time and the data is entered on Form XI. A plot is made from the data and attached to the Form XI. K_{eq} is calculated on Form XI and the results are contrasted with the expected value of Henry's law obtained from Form IX. If the comparison is satisfactory, the stripping constant is calculated from K_{eq}, completing Form XI. The values of K_{eq} may differ because the theoretical value of K_{eq} may not be

applicable to the system of interest. If the comparison of the calculated K_{eq} from the form and the expected value of Henry's law is unsatisfactory, Form X can alternatively be used to validate K_{eq}. If the aerated reactor is demonstrated to not be at equilibrium, either modify the reactor design and/or operation, or use another type of batch test.

The compound-specific biorate constants are then measured using Form XII. The stripping constant that was determined from Form XI and a headspace correction factor of 1 are entered on Form XII. The aerated reactor biotest may then be run, measuring concentrations of each compound of interest as a function of time. If headspace concentrations are measured instead of liquid concentrations, then the corresponding liquid concentrations are calculated from the headspace measurements using the K_{eq} determined on Form XI and entered on Form XII.

The concentration data on Form XII may contain scatter that can adversely influence the data interpretation. It is possible to curve fit the concentration data and enter the concentrations on the fitted curve instead of the actual data. If curve fitting is used, the curve-fitting procedure must be based upon the Equation App. C-4. When curve fitting is used, it is necessary to attach a plot of the actual data and the fitted curve to Form XII.

If the stripping rate constant is relatively large when compared to the biorate at low concentrations, it may be difficult to obtain accurate evaluations of the first-order

biorate constant. In these cases, either reducing the stripping rate constant by lowering the aeration rate, or increasing the biomass concentrations should be considered.

The final result of the batch testing is the measurement of a biorate that can be used to estimate the fraction biodegraded, f_{bio}. The number transferred to Form III is obtained from Form XII, line 9.

2. Sealed Reactor Test. This test uses a closed system to prevent losses of the test compound by volatilization. This test may be conducted using a serum bottle or a sealed draft tube reactor (for an example see Figure 3 of Appendix C). Since no air is supplied, it is necessary to ensure that sufficient oxygen is present in the system. The DO concentration in the system must not fall below 2 mg/liter so that the biodegradation observed will not be DO-limited. As an alternative, oxygen may be supplied by electrolysis as needed to maintain the DO concentration above 2 mg/liter. The reactor contents must be uniformly mixed, by stirring or agitation using a shaker or similar apparatus. The test mixture (or compound) of interest is injected into the reactor and the concentration is monitored over time. A minimum of six samples shall be taken over the period of the test. However, it is necessary to monitor the concentration until it falls below the LOQ.

The equilibrium assumption must be verified for the batch reactor system. In this case, K_{eq} may be determined by simultaneously measuring gas and liquid phase concentrations at

different times within a given experiment. A constant ratio of gas/liquid concentrations indicates that equilibrium conditions are present and K_{eq} is not a function of concentration. This ratio is then taken as the K_{eq} for the specific compound in the test. It is not necessary to measure K_{eq} for each experiment. If the ratio is not constant, the equilibrium assumption is not valid and it is necessary to (1) increase mixing energy for the system and retest for the equilibrium assumption, or (2) use a different type of test (for example, a collapsible volume reactor).

The concentration of a compound decreases in the bioreactor due to biodegradation according to equation App. C-5:

$$\frac{ds}{dt} = \left[\frac{-V_l}{V_g K_{eq} + V_l}\right]\left[\left(\frac{Q_m X}{K_s + s}\right) s\right] \qquad \text{(Eqn App. C-5)}$$

where:

s = test compound concentration (mg/liters)

V_l = the average liquid volume in the reactor (liters)

V_g = the average gas volume in the reactor (liters)

Q_m = maximum rate of substrate removal (mg/g ML VSS/hr)

K_{eq} = Henry's Law constant determined for the test, (mg/liter gas)/(mg/liter liquid)

K_S = Monod biorate constant at one-half the maximum rate (mg/liter)

t = time (hours)

X = biomass concentration (g ML VSS/liter)

S_o = test compound concentration at time t=0

Equation App. C-5 can be solved analytically to give:

$$t = \frac{-(V_s K_{eq} + V_l)}{V_l Q_m X} [(S - S_0) + K_s \ln(\frac{S}{S_0})] \quad \text{(Eqn App. C-6)}$$

This equation is used along with the substrate concentration versus time data to determine the best fit parameters (Q_m and K_S) to describe the biodegradation process in the sealed reactor.

If the sealed reactor test is used, Form X is used to determine the headspace correction factor. The disappearance of a compound in the sealed reactor test is slowed because a fraction of the compound is not available for biodegradation because it is present in the headspace. If the compound is almost entirely in the liquid phase, the headspace correction factor is approximately one. If the headspace correction factor is substantially less than one, improved mass transfer or reduced headspace may improve the accuracy of the sealed reactor test. A preliminary sealed reactor test must be conducted to test the equilibrium assumption. As the compound of interest is degraded, simultaneous headspace and liquid samples should be collected and Form X should be used to evaluate K_{eq}. The ratio of headspace to liquid concentrations must be constant in order to confirm that equilibrium conditions exist. If equilibrium conditions are not present, additional mixing or an alternate reactor configuration may be required.

The compound-specific biorate constants are then calculated using Form XII. For the sealed reactor test, a stripping rate constant of zero and the headspace correction factor that was determined from Form X are entered on Form XII. The sealed reactor test may then be run, measuring the concentrations of each compound of interest as a function of time. If headspace concentrations are measured instead of liquid concentrations, then the corresponding liquid concentrations are calculated from the headspace measurements using K_{eq} from Form X and entered on Form XII.

The concentration data on Form XII may contain scatter that can adversely influence the data interpretation. It is possible to curve fit the concentration data and enter the concentrations on the fitted curve instead of the actual data. If curve fitting is used, the curve-fitting procedure must be based upon Equation App. C-6. When curve fitting is used, it is necessary to attach a plot of the actual data and the fitted curve to Form XII.

If a sealed collapsible reactor is used that has no headspace, the headspace correction factor will equal 1, but the stripping rate constant may not equal 0 due to diffusion losses through the reactor wall. The ratio of the rate of loss of compound to the concentration of the compound in the reactor (units of per hour) must be evaluated. This loss ratio has the same units as the stripping rate constant and may be entered as the stripping rate constant on line 1 of Form XII.

If the loss due to diffusion through the walls of the

collapsible reactor is relatively large when compared to the biorate at low concentrations, it may be difficult to obtain accurate evaluations of the first-order biorate constant. In these cases, either replacing the materials used to construct the reactor with materials of low permeability or increasing the biomass concentration should be considered.

The final result of the batch testing is the measurement of a biorate that can be used to estimate the fraction biodegraded, f_{bio}. The number transferred to Form III is obtained from Form XII, line 9.

The number on Form XII line 9 will equal the Monod first-order biorate constant if the full-scale system is operated in the first-order range. If the full-scale system is operated at concentrations above that of the Monod first-order range, the value of the number on line 9 will be somewhat lower than the Monod first-order biorate constant. With supporting biorate data, the Monod model used in Form XII may be used to estimate the effective biorate constant K1 for use in Form III.

If a reactor with headspace is used, analysis of the data using equation App. C-6 is valid only if V_l and V_g do not change more than 10% (i.e., they can be approximated as constant for the duration of the test). Since biodegradation is occurring only in the liquid, as the liquid concentration decreases it is necessary for mass to transfer from the gas to the liquid phase. This may require vigorous mixing and/or reducing the volume in the headspace of the reactor.

If there is no headspace (e.g., a collapsible reactor), equation App. C-6 is independent of V_l and there are no restrictions on the liquid volume. If a membrane or bag is used as the collapsible-volume reactor, it may be important to monitor for diffusion losses in the system. To determine if there are losses, the bag should be used without biomass and spiked with the compound(s) of interest. The concentration of the compound(s) in the reactor should be monitored over time. The data are analyzed as described above for the sealed reactor test.

3. Quality Control/Quality Assurance (QA/QC). A QA/QC plan outlining the procedures used to determine the biodegradation rate constants shall be prepared and a copy maintained at the source. The plan should include, but may not be limited to:

1. A description of the apparatus used (e.g., size, volume, method of supplying air or oxygen, mixing, and sampling procedures) including a simplified schematic drawing.

2. A description of how biomass was sampled from the activated sludge unit.

3. A description of how biomass was held prior to testing (age, etc.)

4. A description of what conditions (DO, gas-liquid equilibrium, temperature, etc.) are important, what the target values are, how the factors were controlled, and how well they were controlled.

5. A description of how the experiment was conducted, including preparation of solutions, dilution procedures,

sampling procedures, monitoring of conditions, etc.

6. A description of the analytical instrumentation used, how the instruments were calibrated, and a summary of the precision for that equipment.

7. A description of the analytical procedures used. If appropriate, reference to an ASTM, EPA or other procedure may be used. Otherwise, describe how the procedure is done, what is done to measure precision, accuracy, recovery, etc., as appropriate.

8. A description of how data are captured, recorded, and stored.

9. A description of the equations used and their solutions, including a reference to any software used for calculations and/or curve-fitting.

IV. Calculation of F_{bio}

At this point, the individual f_{bio}s determined by the previously explained procedures must be summed to obtain the total F_{bio}. To determine the F_{bio}, multiply each compound specific f_{bio} by the compound-specific average mass flow rate of the organic compound in the wastewater stream (see regulation for instruction on calculation of average mass flow rate). Sum these products and divide by the total wastewater stream average mass flow rate of organic compounds.

M = compound specific average mass flow rate of the organic compounds in the wastewater(Mg/Yr)

$$F_{bio} = \frac{\sum_{i=1}^{n} (f_{bio^i} \times M_i)}{\sum_{i=1}^{n} M_i} \qquad \text{(Eqn App. C-7)}$$

n = number of organic compounds in the wastewater

The F_{bio} is then used in the applicable compliance equations in the regulation to determine if biodegradation may be used to comply with the treatment standard without covering and venting to an air pollution control device.

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TABLE I

	Compound	H_L @ 25°C (atm/mole frac)	H_L @ 100°C (atm/mole frac)
1	Acetaldehyde	4.87e+00	5.64e+01
3	Acetonitrile	1.11e+00	1.78e+01
4	Acetophenone	5.09e-01	2.25e+01
5	Acrolein	4.57e+00	6.61e+01
8	Acrylonitrile	5.45e+00	6.67e+01
9	Allyl chloride	5.15e+02	2.26e+03
10	Aniline	9.78e-02	1.42e+00
12	Benzene	3.08e+02	1.93e+03
14	Benzyl chloride	1.77e+01	2.88e+02
15	Biphenyl	2.27e+01	1.27e+03
17	Bromoform	2.96e+01	3.98e+02
18	1,3-Butadiene	3.96e+03	1.56e+04
20	Carbon disulfide	1.06e+03	3.60e+03
21	Carbon tetrachloride	1.68e+03	1.69e+04
23	2-Chloroacetophenone	4.84e-02	1.43e+01
24	Chlorobenzene	2.09e+02	3.12e+03
25	Chloroform	2.21e+02	1.34e+03
26	Chloroprene	5.16e+01	1.74e+02
29	o-Cresol	9.12e-02	2.44e+01
31	Cumene	7.28e+02	7.15e+03
32	1,4-Dichlorobenzene(p)	1.76e+02	1.95e+03
33	Dichloroethyl ether	1.14e+00	3.57e+01
34	1,3-Dichloropropene	1.97e+02	1.44e+03
36	N,N-Dimethylaniline	7.70e-01	5.67e+02
37	Diethyl sulfate	3.41e-01	4.22e+01
38	3,3′-Dimethylbenzidine	7.51e-05	5.09e-01
40	1,1-Dimethylhydrazine	9.11e-02	1.57e+01
42	Dimethyl sulfate	2.23e-01	1.43e+01

	Compound	H_L @ 25°C (atm/mole frac)	H_L @ 100°C (atm/mole frac)
43	2,4-Dinitrophenol	2.84e-01	1.50e+02
44	2,4-Dinitrotoluene	4.00e-01	9.62e+00
45	1,4-Dioxane	3.08e-01	9.53e+00
47	Epichlorohydrin	1.86e+00	4.34e+01
48	Ethyl acrylate	1.41e+01	3.01e+02
49	Ethylbenzene	4.38e+02	4.27e+03
50	Ethyl chloride(chloroethane)	6.72e+02	3.10e+03
51	Ethylene dibromide	3.61e+01	5.15e+02
52	Ethylene dichloride (1,2-Dichloroethane)	6.54e+01	5.06e+02
54	Ethylene oxide	1.32e+01	9.09e+01
55	Ethylidene dichloride (1,1-Dichloroethane)	3.12e+02	2.92e+03
57	Ethylene glycol dimethyl ether	1.95e+00	4.12e+01
60	Ethylene glycol monoethyl ether acetate	9.86e-02	6.03e+00
62	Ethylene glycol monomethyl ether acetate	1.22e-01	6.93e+00
64	Diethylene glycol dimethyl ether	8.38e-02	4.69e+00
69	Diethylene glycol diethyl ether	1.19e-01	7.71e+00
72	Ethylene glycol monobutyl ether acetate	2.75e-01	2.50e+01
73	Hexachlorobenzene	9.45e+01	2.57e+04
74	Hexachlorobutadiene	5.72e+02	6.92e+03
75	Hexachloroethane	4.64e+02	7.49e+04
76	Hexane	4.27e+04	9.44e+04
78	Isophorone	3.68e-01	1.68e+01
80	Methanol	2.89e-01	7.73e+00

	Compound	H_L @ 25°C (atm/mole frac)	H_L @ 100°C (atm/mole frac)
81	Methyl bromide (Bromomethane)	3.81e+02	2.12e+03
82	Methyl chloride (Chloromethane)	4.90e+02	2.84e+03
83	Methyl chloroform (1,1,1-Trichloroethane)	9.67e+02	5.73e+03
84	Methyl ethyl ketone (2-Butanone)	7.22e+00	5.92e+01
86	Methyl isobutyl ketone (Hexone)	2.17e+01	3.72e+02
88	Methyl methacrylate	7.83e+00	9.15e+01
89	Methyl tert-butyl ether	3.08e+01	2.67e+02
90	Methylene chloride (Dichloromethane)	1.64e+02	9.15e+02
93	Naphthalene	2.68e+01	7.10e+02
94	Nitrobenzene	1.33e+00	2.80e+01
96	2-Nitropropane	6.61e+00	8.76e+01
99	Phosgene	7.80e+02	3.51e+03
102	Propionaldehyde	3.32e+00	1.42e+02
103	Propylene dichloride	1.59e+02	1.27e+03
104	Propylene oxide	1.98e+01	1.84e+02
106	Styrene	1.45e+02	1.72e+03
107	1,1,2,2-Tetrachloroethane	1.39e+01	1.99e+02
108	Tetrachloroethylene (Perchloroethylene)	9.83e+02	1.84e+04
109	Toluene	3.57e+02	2.10e+03
112	o-Toluidine	1.34e-01	1.15e+01
113	1,2,4-Trichlorobenzene	1.07e+02	1.04e+03
114	1,1,2-Trichloroethane	4.58e+01	5.86e+02
115	Trichloroethylene	5.67e+02	7.66e+03
116	2,4,5-Trichlorophenol	4.84e-01	6.27e+01

	Compound	H_L @ 25°C (atm/mole frac)	H_L @ 100°C (atm/mole frac)
117	Triethylamine	6.94e+00	2.57e+02
118	2,2,4-Trimethylpentane	1.85e+05	9.74e+05
119	Vinyl acetate	2.82e+01	2.80e+02
120	Vinyl chloride	1.47e+03	6.45e+03
121	Vinylidene chloride (1,1-Dichloroethylene)	1.44e+03	1.40e+04
123	m-Xylene	4.13e+02	3.25e+03
124	o-Xylene	2.71e+02	2.55e+03
125	p-Xylene	4.13e+02	3.20e+03