Subpart H - National Emission Standards for Organic Hazardous Air Pollutants for Equipment Leaks.

31. Section 63.161 is amended by adding the definition for "combustion device"; revising the definitions of "control device" and "first attempt at repair"; adding the definitions for "fuel gas," fuel gas system," "on-site or on site," "recapture device," and "recovery device"; revising the definition for "repaired" adding the definition for "routed to a process or route to a process" to read as follows:

§63.161 Definitions.

*   *   *   *   *

Combustion device means an individual unit of equipment, such as a flare, incinerator, process heater, or boiler, used for the combustion of organic hazardous air pollutant emissions.

*   *   *   *   *

Control device means any equipment used for recovering, recapturing, or oxidizing organic hazardous air pollutant vapors. Such equipment includes, but is not limited to, absorbers, carbon adsorbers, condensers, flares, boilers, and process heaters.

*   *   *   *   *

First attempt at repair means to take action for the purpose of stopping or reducing leakage of organic material to the atmosphere, followed by monitoring as specified in

§63.180(b) and (c), as appropriate, to verify whether the
leak is repaired, unless the owner or operator determines by
other means that the leak is not repaired.

*   *   *   *   *

Fuel gas means gases that are combusted to derive
useful work or heat.

Fuel gas system means the offsite and onsite piping and
control system that gathers gaseous stream(s) generated by
onsite operations, may blend them with other sources of gas,
and transports the gaseous stream for use as fuel gas in
combustion devices or in in-process combustion equipment
such as furnaces and gas turbines, either singly or in
combination.

*   *   *   *   *

On-site or On site means, with respect to records
required to be maintained by this subpart, that the records
are stored at a location within a major source which
encompasses the affected source. On-site includes, but is
not limited to, storage at the chemical manufacturing
process unit to which the records pertain, or storage in
central files elsewhere at the major source.

*   *   *   *   *

Recapture device means an individual unit of equipment
capable of and used for the purpose of recovering chemicals,
but not normally for use, reuse, or sale. Recapture devices

include, but are not limited to, absorbers, carbon adsorbers, and condensers.

Recovery device means an individual unit of equipment capable of and normally used for the purpose of recovering chemicals for fuel value (i.e., net positive heating value), use, reuse, or for sale for fuel value, use or reuse. Recovery devices include, but are not limited to, absorbers, carbon adsorbers, and condensers. For purposes of the monitoring, recordkeeping, and reporting requirements of this subpart, recapture devices are considered recovery devices.

Repaired means that equipment (1) is adjusted, or otherwise altered, to eliminate a leak as defined in the applicable sections of this subpart, and (2) unless otherwise specified in applicable provisions of this subpart, is monitored as specified in §63.180(b) and (c), as appropriate, to verify that emissions from the equipment are below the applicable leak definition.

Routed to a process or route to a process means the emissions are conveyed by hard-piping or a closed vent system to any enclosed portion of a process unit where the emissions are predominately recycled and/or consumed in the same manner as a material that fulfills the same function in the process; and/or transformed by chemical reaction into materials that are not organic hazardous air pollutants; and/or incorporated into a product; and/or recovered.

*   *   *   *   *

32. Section 63.162 is amended by revising paragraphs (f)(2) and (f)(3); adding paragraphs (g) and (h) to read as follows:

§63.162 Standards: General.

*   *   *   *   *

(f) * * *

(2) The identification on a valve may be removed after it has been monitored as specified in §§63.168(f)(3), and 63.175(e)(7)(i)(D) of this subpart, and no leak has been detected during the follow-up monitoring. If the owner or operator elects to comply using the provisions of §63.174(c)(1)(i) of this subpart, the identification on a connector may be removed after it is monitored as specified in §63.174(c)(1)(i) and no leak is detected during that monitoring.

(3) The identification which has been placed on equipment determined to have a leak, except for a valve or for a connector that is subject to the provisions of §63.174(c)(1)(i), may be removed after it is repaired.

(g) Except as provided in paragraph (g)(1) of this section, all terms in this subpart that define a period of time for completion of required tasks (e.g., weekly, monthly, quarterly, annual), refer to the standard calendar periods unless specified otherwise in the section or subsection that imposes the requirement.

(1) If the initial compliance date does not coincide with the beginning of the standard calendar period, an owner or operator may elect to utilize a period beginning on the compliance date, or may elect to comply in accordance with the provisions of paragraphs (g)(2) or (g)(3) of this section.

(2) Time periods specified in this subpart for completion of required tasks may be changed by mutual agreement between the owner or operator and the Administrator, as specified in subpart A of this part. For each time period that is changed by agreement, the revised period shall remain in effect until it is changed. A new request is not necessary for each recurring period.

(3) Except as provided in paragraph (g)(1) or (g)(2) of this section, where the period specified for compliance is a standard calendar period, if the initial compliance date does not coincide with the beginning of the calendar period, compliance shall be required according to the schedule specified in paragraphs (g)(3)(i) or (g)(3)(ii) of this section, as appropriate.

(i) Compliance shall be required before the end of the standard calendar period within which the compliance deadline occurs, if there remain at least 3 days for tasks that must be performed weekly, at least 2 weeks for tasks that must be performed monthly, at least 1 month for tasks

that must be performed each quarter, or at least 3 months
for tasks that must be performed annually; or

(ii) In all other cases, compliance shall be required
before the end of the first full standard calendar period
after the period within which the initial compliance
deadline occurs.

(4) In all instances where a provision of this subpart
requires completion of a task during each of multiple
successive periods, an owner or operator may perform the
required task at any time during each period, provided the
task is conducted at a reasonable interval after completion
of the task during the previous period.

(h) In all cases where the provisions of this subpart
require an owner or operator to repair leaks by a specified
time after the leak is detected, it is a violation of this
subpart to fail to take action to repair the leaks within
the specified time. If action is taken to repair the leaks
within the specified time, failure of that action to
successfully repair the leak is not a violation of this
subpart. However, if the repairs are unsuccessful, a leak
is detected and the owner or operator shall take further
action as required by applicable provisions of this subpart.

33. Section 63.163 is amended by revising paragraphs
(e)(1)(ii) and (g) to read as follows:

§63.163 Standards: Pumps in light liquid service.

* * * * *

(e) * * *

(1) * * *

(ii) Equipped with a barrier fluid degassing reservoir that is routed to a process or fuel gas system or connected by a closed-vent system to a control device that complies with the requirements of §63.172 of this subpart; or

* * * * *

(g) Any pump equipped with a closed-vent system capable of capturing and transporting any leakage from the seal or seals to a process or to a fuel gas system or to a control device that complies with the requirements of §63.172 of this subpart is exempt from the requirements of paragraphs (b) through (e) of this section.

* * * * *

34. Section 63.164 is amended by revising paragraphs (b)(2) and (h) to read as follows:

§63.164 Compressors.

* * * * *

(b) * * *

(2) Equipped with a barrier fluid system degassing reservoir that is routed to a process or fuel gas system or connected by a closed-vent system to a control device that complies with the requirements of §63.172 of this subpart; or

* * * * *

(h) A compressor is exempt from the requirements of paragraphs (a) through (f) of this section if it is equipped with a closed-vent system to capture and transport leakage from the compressor drive shaft seal back to a process or a fuel gas system or to a control device that complies with the requirements of §63.172 of this subpart.

* * * * *

35. Section 63.165 is amended by revising paragraph (c) to read as follows:

§63.165 Standards: Pressure relief devices in gas/vapor service.

* * * * *

(c) Any pressure relief device that is routed to a process or fuel gas system or equipped with a closed-vent system capable of capturing and transporting leakage from the pressure relief device to a control device as described in §63.172 of this subpart is exempt from the requirements of paragraphs (a) and (b) of this section.

* * * * *

36. Section 63.168 is amended by revising the meaning of %V_L in paragraph (e)(1) and revising paragraph (f)(3) to read as follows:

§63.168 Standards: Valves in gas/vapor service and in light liquid service.

* * * * *

(e)(1) * * *

$\%V_L$ = Percent leaking valves as determined through periodic monitoring required in paragraphs (b) through (d) of this section.

* * * * *

(f) * * *

(3) When a leak has been repaired, the valve shall be monitored at least once within the first 3 months after its repair.

(i) The monitoring shall be conducted as specified in §63.180(b) and (c), as appropriate, to determine whether the valve has resumed leaking.

(ii) Periodic monitoring required by paragraphs (b) through (d) of this section may be used to satisfy the requirements of this paragraph (f)(3), if the timing of the monitoring period coincides with the time specified in paragraph (f)(3) of this section. Alternatively, other monitoring may be performed to satisfy the requirements of this paragraph (f)(3) of this section, regardless of whether the timing of the monitoring period for periodic monitoring coincides with the time specified in paragraph (f)(3) of this section.

(iii) If a leak is detected by monitoring that is conducted pursuant to paragraph (f)(3) of this section, the owner or operator shall follow the provisions of paragraphs (f)(3)(iii)(A) and (f)(3)(iii)(B) of this

section, to determine whether that valve must be counted as a leaking valve for purposes of §63.168(e) of this subpart.

(A) If the owner or operator elected to use periodic monitoring required by paragraphs (b) through (d) of this section to satisfy the requirements of paragraph (f)(3) of this section, then the valve shall be counted as a leaking valve.

(B) If the owner or operator elected to use other monitoring, prior to the periodic monitoring required by paragraphs (b) through (d) of this section, to satisfy the requirements of paragraph (f)(3) of this section, then the valve shall be counted as a leaking valve unless it is repaired and shown by periodic monitoring not to be leaking.

*   *   *   *   *

37. Section 63.169 is amended by revising paragraph (c)(3) to read as follows:

§63.169 Standards: Pumps, valves, connectors, and agitators in heavy liquid service; instrumentation systems; and pressure relief devices in liquid service.

*   *   *   *   *

(c) *   *   *

(3) For equipment identified in paragraph (a) of this section that is not monitored by the method specified in §63.180(b), repaired shall mean that the visual, audible, olfactory, or other indications of a leak to the atmosphere have been eliminated; that no bubbles are observed at

potential leak sites during a leak check using soap

solution; or that the system will hold a test pressure.

*   *   *   *   *

38. Section 63.172 is amended by revising paragraphs

(b), (c), (h)(2), and (j)(2), and adding paragraph (n) to

read as follows:

§63.172 Standards: Closed-vent systems and control

devices.

*   *   *   *   *

(b) Recovery or recapture devices (e.g., condensers

and adsorbers) shall be designed and operated to recover the

organic hazardous air pollutant emissions or volatile

organic compounds emissions vented to them with an

efficiency of 95 percent or greater, or to an exit

concentration of 20 parts par million by volume, whichever

is less stringent. The 20 parts per million by volume

performance standard is not applicable to the provisions of

§63.179.

(c) Enclosed combustion devices shall be designed and

operated to reduce the organic hazardous air pollutant

emissions or volatile organic compounds emissions vented to

them with an efficiency of 95 percent or greater, or to an

exit concentration of 20 parts per million by volume, on a

dry basis, corrected to 3 percent oxygen, whichever is less

stringent, or to provide a minimum residence time of

0.50 seconds at a minimum temperature of 760° C.

* * * * *

(h) * * *

(2) Repair shall be completed no later than
15 calendar days after the leak is detected, except as
provided in paragraph (i) of this section.

* * * * *

(j) * * *

(2) Secure the bypass line valve in the non-diverting
position with a car-seal or a lock-and-key type
configuration. A visual inspection of the seal or closure
mechanism shall be performed at least once every month to
ensure the valve is maintained in the non-diverting position
and the vent stream is not diverted through the bypass line.

* * * * *

(n) After the compliance dates specified in §63.100 of
subpart F of this part, the owner or operator of any control
device subject to this subpart that is also subject to
monitoring, recordkeeping, and reporting requirements in 40
CFR part 264, subpart BB, or is subject to monitoring and
recordkeeping requirements in 40 CFR part 265, subpart BB,
may elect to comply either with the monitoring,
recordkeeping, and reporting requirements of this subpart,
or with the monitoring, recordkeeping, and reporting
requirements in 40 CFR parts 264 and/or 265, as described in
this paragraph, which shall constitute compliance with the
monitoring, recordkeeping and reporting requirements of this

subpart. The owner or operator shall identify which option has been chosen, in the next periodic report required by §63.182(d).

39. Section 63.173 is amended by revising paragraphs (d)(1)(ii), (f), and (g) to read as follows:

§63.173 Standards: Agitators in gas/vapor service and in light liquid service.

*   *   *   *   *

(d) *   *   *

(1) *   *   *

(ii) Equipped with a barrier fluid degassing reservoir that is routed to a process or fuel gas system or connected by a closed-vent system to a control device that complies with the requirements of §63.172 of this subpart; or

*   *   *   *   *

(f) Any agitator equipped with a closed-vent system capable of capturing and transporting any leakage from the seal or seals to a process or fuel gas system or to a control device that complies with the requirements of §63.172 of this subpart is exempt from the requirements of paragraphs (a) through (c) of the section.

(g) Any agitator that is located within the boundary of an unmanned plant site is exempt from the weekly visual inspection requirement of paragraphs (b)(1) and (d)(4) of this section, and the daily requirements of paragraph (d)(5)

of this section, provided that each agitator is visually
inspected as often as practical and at least monthly.

*   *   *   *   *

40.   Section 63.174 is amended by revising paragraphs
(c)(1)(i), (c)(1)(ii), the introductory text in paragraph
(c)(2), revising paragraph (c)(2)(ii); adding paragraphs
(c)(2)(iii) and (c)(2)(iv); removing and reserving paragraph
(e); revising paragraph (h)(2); and revising paragraphs
(i)(1) and (i)(2) to read as follows:

§63.174 Standards: Connectors in gas/vapor service and in
light liquid service.

*   *   *   *   *

(c)(1)(i) Except as provided in paragraph (c)(1)(ii)
of this section, each connector that has been opened or has
otherwise had the seal broken shall be monitored for leaks
when it is reconnected or within the first 3 months after
being returned to organic hazardous air pollutants service.
If the monitoring detects a leak, it shall be repaired
according to the provisions of paragraph (d) of this
section, unless it is determined to be nonrepairable, in
which case it is counted as a nonrepairable connector for
the purposes of paragraph (i)(2) of this section.

(ii) As an alternative to the requirements in
paragraph (c)(1)(i) of this section, an owner or operator
may choose not to monitor connectors that have been opened
or otherwise had the seal broken. In this case, the owner

or operator may not count nonrepairable connectors for the purposes of paragraph (i)(2) of this section. The owner or operator shall calculate the percent leaking connectors for the monitoring periods described in paragraph (b) of this section, by setting the nonrepairable component, C_{AN}, in the equation in paragraph (i)(2) of this section to zero for all monitoring periods.

*   *   *   *   *

(2) As an alternative to the requirements of paragraph (b)(3) of this section, each screwed connector 2 inches or less in nominal inside diameter installed in a process unit before the dates specified in paragraphs (2)(iii) or (2)(iv) of this section may:

*   *   *   *   *

(ii) Be monitored for leaks within the first 3 months after being returned to organic hazardous air pollutants service after having been opened or otherwise had the seal broken. If that monitoring detects a leak, it shall be repaired according to the provisions of paragraph (d) of this section.

(iii) For sources subject to subparts F and I of this part, the provisions of paragraph (2) of this section apply to screwed connectors installed before December 31, 1992.

(iv) For sources not identified in paragraph (2)(iii) of this section, the provisions of paragraph (2) of this section apply to screwed connectors installed before the

date of proposal of the applicable subpart of this part that references this subpart.

*   *   *   *   *

    (e)   [Reserved]

*   *   *   *   *

    (h)   *   *   *

    (2)   If any inaccessible or ceramic or ceramic-lined connector is observed by visual, audible, olfactory, or other means to be leaking, the leak shall be repaired as soon as practicable, but no later than 15 calendar days after the leak is detected, except as provided in §63.171 of this subpart and paragraph (g) of this section.

*   *   *   *   *

    (i)   *   *   *

    (1)   For the first monitoring period, use the following equation:

$$\% \ C_L = C_L / (C_t + C_C) \times 100$$

where:

    $\% \ C_L$ =   Percent leaking connectors as determined through periodic monitoring required in paragraphs (a) and (b) of this section.

    C_L =   Number of connectors measured at 500 parts per million or greater, by the method specified in §63.180(b) of this subpart.

    C_t =   Total number of monitored connectors in the process unit.

C_C = Optional credit for removed connectors = 0.67 x net (i.e., total removed - total added) number of connectors in organic hazardous air pollutants service removed from the process unit after the compliance date set forth in the applicable subpart for existing process units, and after the date of initial start-up for new process units. If credits are not taken, then C_C = 0.

(2) For subsequent monitoring periods, use the following equation:

$$\% \; C_L = [(C_L - C_{AN}) / (C_t + C_C)] \; x \; 100$$

where:

$\% \; C_L$ = Percent leaking connectors as determined through periodic monitoring required in paragraphs (a) and (b) of this section.

C_L = Number of connectors, including nonrepairables, measured at 500 parts per million or greater, by the method specified in §63.180(b) of this subpart.

C_{AN} = Number of allowable nonrepairable connectors, as determined by monitoring required in paragraphs (b)(3) and (c) of this section, not to exceed 2 percent of the total connector population, C_t.

C_t = Total number of monitored connectors, including nonrepairables, in the process unit.

C_C = Optional credit for removed connectors = 0.67 x net number (i.e., total removed - total added) of connectors in organic hazardous air pollutants service removed from the process unit after the compliance date set forth in the applicable subpart for existing process units, and after the date of initial start-up for new process units. If credits are not taken, then C_C = 0.

* * * * *

41. Section 63.180 is amended by revising paragraphs (b)(4)(ii), the introductory text in paragraph (c), and paragraph (c)(2) to read as follows:

§63.180 Test methods and procedures.

* * * * *

(b) * * *

(4) * * *

(ii) Mixtures of methane in air at the concentrations specified in paragraphs (b)(4)(ii)(A) through (b)(4)(ii)(C) of this section. A calibration gas other than methane in air may be used if the instrument does not respond to methane or if the instrument does not meet the performance criteria specified in paragraph (b)(2)(i) of this section.

In such cases, the calibration gas may be a mixture of one
or more of the compounds to be measured in air.

(A) For Phase I, a mixture of methane or other
compounds, as applicable, in air at a concentration of
approximately, but less than, 10,000 parts per million.

(B) For Phase II, a mixture of methane or other
compounds, as applicable, and air at a concentration of
approximately, but less than, 10,000 parts per million for
agitators, 5,000 parts per million for pumps, and 500 parts
per million for all other equipment, except as provided in
paragraph (b)(4)(iii) of this section.

(C) For Phase III, a mixture of methane or other
compounds, as applicable, and air at a concentration of
approximately, but less than, 10,000 parts per million
methane for agitators; 2,000 parts per million for pumps in
food/medical service; 5,000 parts per million for pumps in
polymerizing monomer service; 1,000 parts per million for
all other pumps; and 500 parts per million for all other
equipment, except as provided in paragraph (b)(4)(iii) of
this section.

*   *   *   *   *

(c) When equipment is monitored for compliance as
required in §§63.164(i), 63.165(a), and 63.172(f) or when
equipment subject to a leak definition of 500 ppm is
monitored for leaks as required by this subpart, the owner
or operator may elect to adjust or not to adjust the

instrument readings for background. If an owner or operator elects to not adjust instrument readings for background, the owner or operator shall monitor the equipment according to the procedures specified in paragraphs (b)(1) through (b)(4) of this section. In such case, all instrument readings shall be compared directly to the applicable leak definition to determine whether there is a leak. If an owner or operator elects to adjust instrument readings for background, the owner or operator shall monitor the equipment according to the procedures specified in paragraphs (c)(1) through (c)(4) of this section.

* * * * *

(2) The background level shall be determined, using the same procedures that will be used to determine whether the equipment is leaking.

* * * * *

42. Section 63.181 is amended by revising paragraphs (d)(7)(i) and (d)(7)(ii), revising the introductory text in paragraphs (g)(2) and (g)(3), and revising paragraph (i) to read as follows:

§63.181 Recordkeeping requirements.

* * * * *

(d) * * *

(7)(i) Identification, either by list, location (area or grouping), or tagging of connectors that have been opened or otherwise had the seal broken since the last monitoring

period required in §63.174(b) of this subpart, as described in §63.174(c)(1) of this subpart, unless the owner or operator elects to comply with the provisions of §63.174(c)(1)(ii) of this subpart.

(ii) The date and results of monitoring as required in §63.174(c) of this subpart. If identification of connectors that have been opened or otherwise had the seal broken is made by location under paragraph (d)(7)(i) of this section, then all connectors within the designated location shall be monitored.

*   *   *   *   *

(g) * * *

(2) Records of operation of closed-vent systems and control devices, as specified in paragraphs (g)(2)(i) through (g)(2)(iii) of this section.

*   *   *   *   *

(3) Records of inspections of closed-vent systems subject to the provisions of §63.172, as specified in paragraphs (g)(2)(i) through (g)(2)(iii) of this section.

*   *   *   *   *

(i) The owner or operator of equipment in heavy liquid service shall comply with the requirements of either paragraph (i)(1) or (i)(2) of this section, as provided in paragraph (i)(3) of this section.

(1) Retain information, data, and analyses used to determine that a piece of equipment is in heavy liquid service.

(2) When requested by the Administrator, demonstrate that the piece of equipment or process is in heavy liquid service.

(3) A determination or demonstration that a piece of equipment or process is in heavy liquid service shall include an analysis or demonstration that the process fluids do not meet the definition of "in light liquid service." Examples of information that could document this include, but are not limited to, records of chemicals purchased for the process, analyses of process stream composition, engineering calculations, or process knowledge.

* * * * *

43. Section 63.182 is amended by adding paragraph (d)(2)(xvii) to read as follows:

§63.182 Reporting requirements.

* * * * *

(d) * * *

(2) * * *

(xvii) If applicable, the compliance option that has been selected under §63.172(n).

Subpart I--National Emission Standards for Organic Hazardous Air Pollutants for Certain Processes Subject to the Negotiated Regulation for Equipment Leaks

44. Section 63.190 is amended by adding a sentence to the end of paragraph (d) and revising the last sentence in paragraphs (e)(5)(i) and (e)(5)(ii) to read as follows:

§63.190 Applicability and designation of source.

* * * * *

(d) * * * If specific items of equipment, comprising part of a process unit subject to this subpart, are managed by different administrative organizations (e.g., different companies, affiliates, departments, divisions, etc.) those items of equipment may be aggregated with any process unit within the source for all purposes under subpart H, providing there is no delay in the applicable compliance date in paragraph (e) of this section.

(e) * * *

(5)(i) * * * The owner or operator who elects to use this provision shall also comply with the requirements of §63.192(m) of this subpart.

(ii) * * * The owner or operator who elects to use this provision shall also comply with the requirements of §63.192(m) of this subpart.

* * * * *

45. Section 63.191 is amending by adding the definition for "on-site or on site" to read as follows:

§63.191 Definitions.

* * * * *

On-site or On site means, with respect to records required to be maintained by this subpart, that the records are stored at a location within a major source which encompasses the affected source. On-site includes, but is not limited to, storage at the process unit to which the records pertain, or storage in central files elsewhere at the major source.

*   *   *   *   *

46. Section 63.192 is amended by adding two sentences to the end of the introductory text in paragraph (f); revising paragraph (f)(1); adding a sentence to the end of paragraph (f)(2)(iii); revising paragraph (g)(1); and revising paragraph (k) to read as follows:

§63.192 Standard.

*   *   *   *   *

(f) * * * If an owner or operator submits copies of reports to the applicable EPA Regional Office, the owner or operator is not required to maintain copies of reports. If the EPA Regional Office has waived the requirement of §63.10(a)(4)(ii) for submittal of copies of reports, the owner or operator is not required to maintain copies of reports.

(1) All applicable records shall be maintained in such a manner that they can be readily accessed. The most recent 6 months of records shall be retained on site or shall be

accessible from a central location by computer or other means that provides access within 2 hours after a request.

(2) * * *

(iii) * * * These records may take the form of a "checklist," or other form of recordkeeping that confirms conformance with the startup, shutdown, and malfunction plan for the event.

(g) * * *

(1) * * * Submittals shall be sent on or before the specified date.

* * * * *

(k) The owner or operator of a process unit which meets the criteria of §63.190 (c), shall comply with the requirements of either paragraph (k)(1) or (k)(2) of this section.

(1) Retain information, data, and analysis used to determine that the process unit does not have the designated organic hazardous air pollutant present in the process. Examples of information that could document this include, but are not limited to, records of chemicals purchased for the process, analyses of process stream composition, engineering calculations, or process knowledge.

(2) When requested by the Administrator, demonstrate that the chemical manufacturing process unit does not have the designated organic hazardous air pollutant present in the process.

*   *   *   *   *

47. Section 63.193 is amended by revising the text to
read as follows:

§63.193 Delegation of authority.

In delegating implementation and enforcement authority
to a State under section 112(l) of the Clean Air Act, the
authority for §63.177 of subpart H of this part shall be
retained by the Administrator and not transferred to a
State.

48. 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
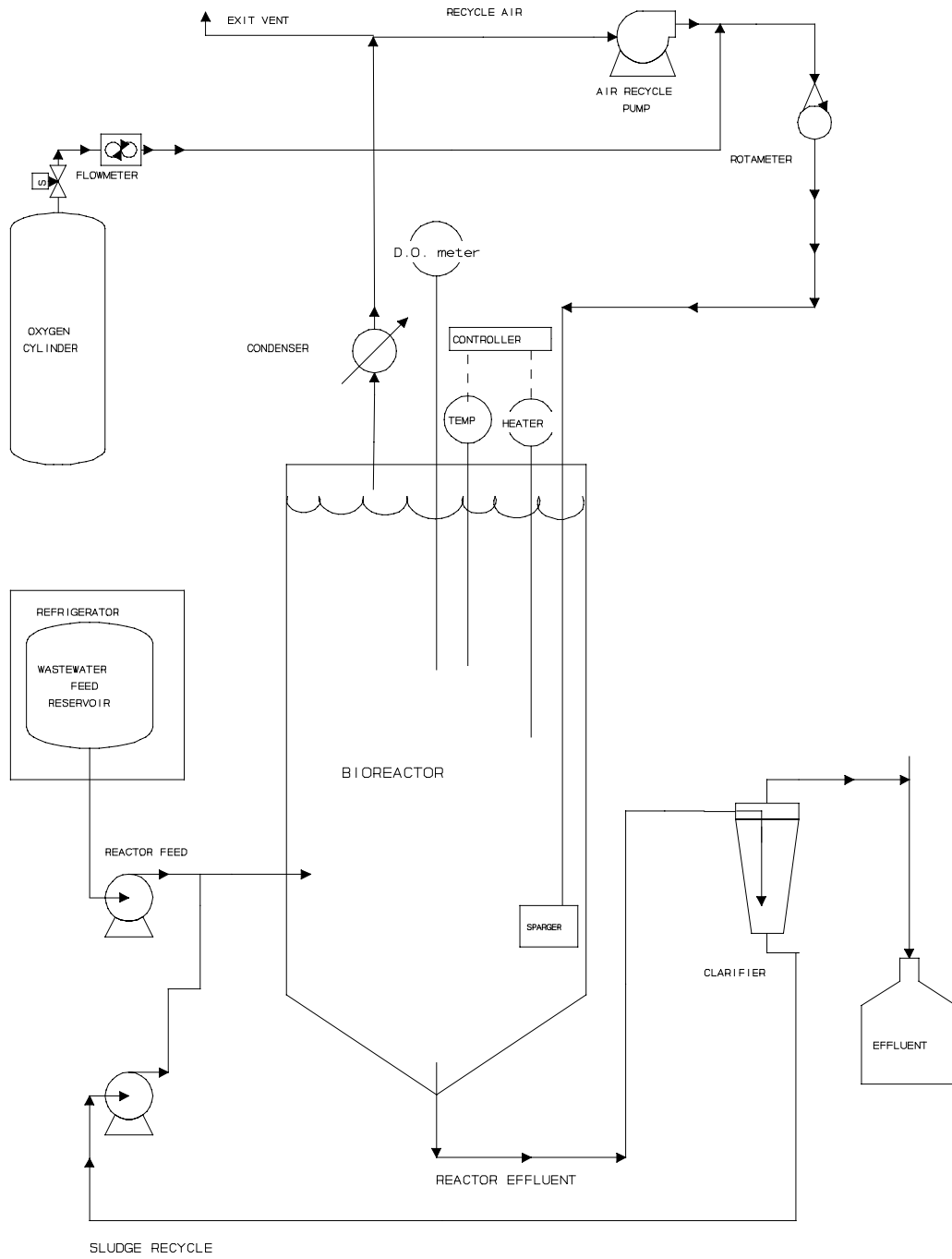
outlet to the benchtop bioreactor are left to the discretion of the source, except where validated methods are available.

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).

EXIT VENT   RECYCLE AIR

AIR RECYCLE
PUMP

ROTAMETER

FLOWMETER

D.O. meter

OXYGEN
CYLINDER

CONDENSER

CONTROLLER

TEMP   HEATER

REFRIGERATOR

WASTEWATER
FEED
RESERVOIR

BIOREACTOR

REACTOR FEED

SPARGER

CLARIFIER

EFFLUENT

REACTOR EFFLUENT

SLUDGE RECYCLE

EPA METHOD 304A VENT BIOREACTOR SYSTEM

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 within 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 within 1.5 mg/L of the target dissolved oxygen concentration; however, for target full-scale activated sludge systems with dissolved oxygen concentrations above 2 mg/L, the dissolved oxygen concentration in the benchtop bioreactor may not drop below 1.5 mg/L. 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 $^{\circ}$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 $^\circ$C, throughout the testing period. Monitor and record

the temperature of the benchtop bioreactor contents at least

to the nearest 0.1 $^\circ$C.

   4.1.1 Wastewater Storage. Collect the wastewater

sample in the 20-L collapsible container. Store the

container at 4 $^\circ$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.

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

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:

$$V_W = V_r \left(\frac{S_m - S_s}{S_m} \right)$$
Eqn 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:

$$V_W = V_r \left(\frac{S_s - S_m}{S_w} \right)$$
Eqn 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)

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

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

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

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

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

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

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

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 °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.
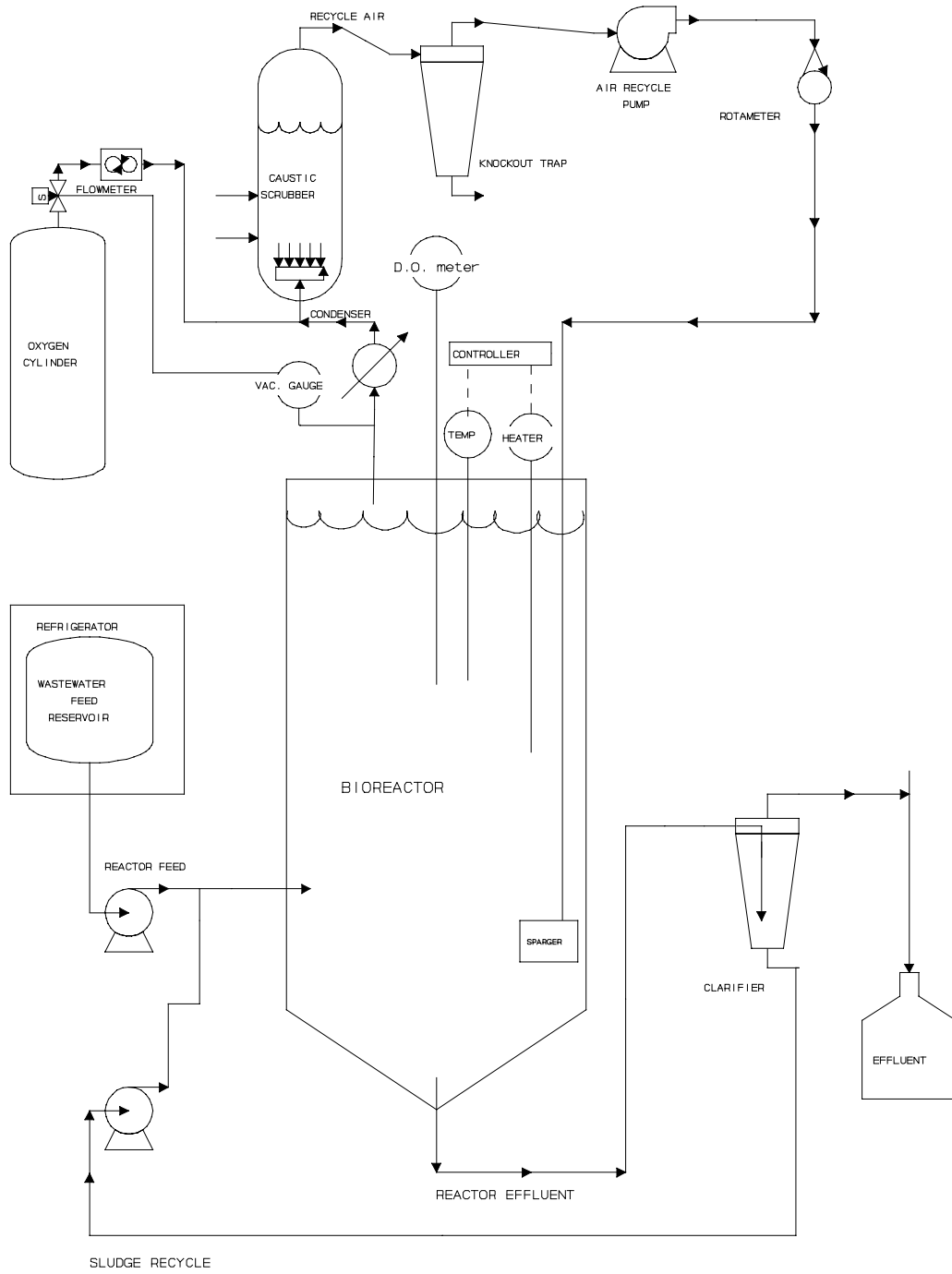
2. Apparatus

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

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TEMP

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REFRIGERATOR

WASTEWATER
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BIOREACTOR

REACTOR FEED

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REACTOR EFFLUENT

SLUDGE RECYCLE

EPA METHOD 304B BIOREACTOR SYSTEM

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 $^{\circ}$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 within 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 within 1.5 mg/L of the target dissolved oxygen concentration; however, for target full-scale activated sludge systems with dissolved oxygen concentrations above 2 mg/L, the dissolved oxygen concentration in the benchtop bioreactor may not drop below 1.5 mg/L. 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.

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

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 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:

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

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:

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

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)

$$t = \frac{V}{Q}$$ Eqn 304B-4

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

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

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

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

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

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

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, 16th Edition, Method 209C, Total Suspended Solids Dried at 103-105°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.

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.

The forms presented in this appendix are designed to address uniform well-mixed or completely mixed systems. Uniform well-mixed or completely mixed systems are biological treatment activated sludge systems where measurements of parameters that indicate performance, e.g., MLVSS, organic compound concentration, and dissolved oxygen, are consistent throughout the system. Systems that are not uniform well-mixed systems should be subdivided into a series of zones that have uniform characteristics within each zone.

The number of zones required to characterize a biological treatment system will depend on the design and operation of the treatment system. The number of zones could vary from one in a well-mixed conventional activated sludge tank to numerous zones in a large surface-aerated impoundment system. Each zone should then be modeled as a

separate unit. The amount of air emissions and biodegradation from the modeling of these separate zones can then be added to reflect the entire system.

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 3 may only be used on a uniform well-mixed or
completely mixed system. 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 EPA 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. This procedure may only be used on a uniform well-mixed or completely mixed system. 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:

$$\frac{S_o}{X_o} = \frac{S_i}{1.42\ X}$$

(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. <u>Aerated Reactor Test</u>. 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:

$$-t = \frac{VK_s}{A} \ln\left(\frac{s}{s_0}\right) + \frac{Q_m XV^2}{AB} \ln\left(\frac{A+Bs}{A+Bs_0}\right)$$ (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. <u>Sealed Reactor Test</u>. 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:

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

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 MLVSS/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 MLVSS/liter)

s_o =   test compound concentration at time t=0

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

$$t = \frac{-(V_s K_{eq} + V_l)}{V_l Q_m X} [(s - s_0) + K_s \ln(\frac{s}{s_0})]$$ (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. <u>Quality Control/Quality Assurance (QA/QC)</u>. 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.

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

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

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.

<u>References</u>

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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