Designation: D 6776 – 02

Standard Test Method for Determining Anaerobic Biodegradability of Radiolabeled Plastic Materials in a Laboratory-Scale Simulated Landfill Environment[1]

This standard is issued under the fixed designation D 6776; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method is designed to measure the anaerobic biodegradability of a material under conditions that simulate accelerated decomposition in a municipal solid waste (MSW) landfill. The test method requires the use of a ^{14}C-labeled material so that biodegradability can be determined by monitoring for methane ($^{14}CH_4$) and gaseous and aqueous carbon dioxide ($^{14}CO_{2(g)}$ and $^{14}CO_{2(aq)}$), which are the terminal end-products of methanogenic decomposition. Methanogenic conditions typically control decomposition in landfills.

NOTE 1—A more complete description of this decomposition is found in Reference **(3)**.[2]

1.2 This method could be applied to landfills that contain materials other than MSW. ^{14}C-Radiolabeled material will be added to compost such that between 25 μci and 75 μci activity per 2 litres of test refuse results.

NOTE 2—Adding more radiolabel is desirable because, if the material biodegrades, there will be little residual radiolabel left at the end of the decomposition experiment, which is when the refuse is removed from a reactor and analyzed for residual radiolabel to perform a mass balance. In addition, if insufficient radiolabel is added, then CH_4 and $CO_{2(g)}$ production from the added refuse will dilute the $^{14}CH_4$ and $^{14}CO_{2(g)}$ from decomposition of the test material, and the labeled gases may not be detected in the reactor offgas.

1.3 This measure of anaerobic biodegradability in the laboratory represents what will ultimately occur in a landfill over a long period. The test conditions specified here are designed to accelerate refuse decomposition such that the entire decomposition cycle can be completed in six months.

NOTE 3—This cycle may require decades in a landfill depending upon the actual environmental conditions (moisture content, pH, temperature).

1.4 The measured biodegradability obtained here is compared to the biodegradability of both pure and lignified cellulose, which are chemically similar to office paper and newsprint, both of which are routinely buried in landfills.

NOTE 4—The degradability of the referenced compounds is described in References **(2)** and **(5)**.

At this time, there is no standard concerning the extent to which a compound must biodegrade under the test conditions described here to be considered biodegradable. Thus, this test is most appropriately used to measure biodegradability relative to pure and lignified cellulose.

1.5 *The safety problems associated with refuse and radioactivity are not addressed in this standard. It is the responsibility of the user of this standard to establish appropriate safety and health practices. It is also incumbent on the user to conform to all the regulatory requirements, specifically those that relate to the use of open radioactive sources.*

NOTE 5—There are no corresponding ISO standards.

2. Referenced Documents

2.1 *ASTM Standards:*

D 883 Terminology Relating to Plastics[3]

E 170 Terminology Relating to Radiation Measurements and Dosimetry[4]

3. Terminology

3.1 Terminology used in this Standard are defined in Terminology D 883 or Terminology E 170.

3.2 *refuse, n*—waste material for anaerobic decomposition. May be municipal or agricultural in source but not meant to include sludge from water treatment or sewage treatment facilities.

[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.96 on Environmentally Degradable Plastics.

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[2] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[3] *Annual Book of ASTM Standards*, Vol 08.01.

[4] *Annual Book of ASTM Standards*, Vol 12.02.

3.3 *seed, n*—refuse material from an active anaerobic decomposition producing methane; which is used for inoculum of refuse material to undergo anaerobic decomposition.

4. Summary of Test Method

4.1 A ^{14}C-labeled material is added to a mixture of fresh and decomposed refuse in a laboratory reactor. The old refuse serves as a seed to rapidly initiate methanogenesis. The volume of gas produced and the concentrations of $^{14}CH_4$ and $^{14}CO_{2(g)}$ are monitored. In addition, the reactor leachate is monitored for ^{14}C-organics and $^{14}CO_{2(aq)}$. At the conclusion of the refuse decomposition cycle, which typically requires 6 to 9 months, the refuse is removed from the reactor, dried, ground to a fine powder and analyzed for residual ^{14}C by combustion. A mass balance on the added ^{14}C is then conducted.

5. Significance and Use

5.1 This method can be used to assess the anaerobic biodegradability of polymeric components of MSW such as packaging materials and to compare their biodegradability to that of materials routinely buried in landfills such as office paper and newsprint. The procedure can be completed in 6 to 9 months. This timeframe makes it possible to consider waste management during product design. The data from this method makes it possible to characterize the behavior of consumer products at the end of their useful life when they enter the solid waste management system.

5.2 *Limitations*—Because decomposition in this test is accelerated, the results reflect the ultimate biodegradability of a material in a landfill. The actual rate of degradability in a full-scale landfill will be affected by landfill environmental conditions as well as the physical characteristics of the material when actually buried.

6. Apparatus

6.1 Tolerances of 5 % from specification are acceptable unless otherwise stated.

6.2 *Reactor*—A detailed description of the 2-L reactor that was used for this research is described in Annex A1. Alternate reactor designs and sizes are acceptable. The critical criteria for the reactor are the ability (*1*) to obtain a gas-tight seal so that biogas may be collected, (*2*) to maintain anaerobic conditions, (*3*) to sample and recirculate leachate and (*4*) to ensure that there are no interactions between the material to be tested and the reactor system. If a larger system is used, then additional radiolabel should be added so that radiolabeled endproducts are not diluted to below detection by the increased volume of gas produced as the refuse decomposes.

6.3 *Gas Bag*—The gas bag must contain CO_2 and CH_4 while not allowing oxygen entry via diffusion. If a material to be tested may result in the production of volatile intermediates or endproducts, then the gas bag material should not result in sorptive losses for these compounds.

6.4 *pH Meter*.

6.5 *Combustion Furnace*—This consists of a column packed with copper oxide catalyst and a furnace capable of achieving temperatures of 875°C for oxidation of $^{14}CH_4$ to $^{14}CO_2$.

6.6 *Tube Furnace*, capable of achieving temperatures of 875°C. This consists of a steel column (121.9 cm [48 in.] long by 3.8 cm [1.5 in.] inside diameter) packed with copper oxide for oxidation of refuse samples.

6.7 *Ether-based Polyurethane Tubing*.

6.8 *Liquid Scintillation Counter*, with background correction capabilities.

6.9 *Gas Chromatograph (GC)*, equipped with a thermal conductivity detector; a column capable of separating CH_4, CO_2, oxygen (O_2), and nitrogen (N_2); and an integrator.

6.10 *Centrifuge*, equipped with a bucket that can hold 10-mL centrifuge tubes and capable of 3500 rpm.

6.11 *Syringe Pump*.

6.12 *Pressure Gage*.

6.13 *Vacuum Pump*.

6.14 *Wiley Cutting Mill*.

6.15 *Fiberglass Mesh*, standard construction grade.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available **(1)**. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise stated, references to water shall be understood to mean deionized water with a resistance of greater than 10 megohms.

7.3 *Scintillation Cocktail*, capable of dissolving 1 mL of 2N sodium hydroxide (NaOH) without separation into layers or color production, or both.

NOTE 6—Packard Instruments' ULTIMA GOLD® meets this criteria. No other Scintillation reagent tested did.

7.4 2 *N* NaOH.

7.5 0.5 *M* sulfuric acid (H_2SO_4).

8. Hazards

8.1 This practice involves the use of microorganisms and hazardous chemicals that could produce a variety of diseases. Avoid contact with these materials by wearing gloves and other appropriate protective equipment. Use good personal hygiene to minimize exposure, and follow the instructions given in material safety data sheets.

8.2 The simulated-solid-waste mixture could contain sharp objects. Extreme care should be taken when handling this mixture to avoid injury.

9. Procedure

NOTE 7—**Precaution:** Adequate laboratory facilities, such as fume hoods and controlled ventilation, along with safe techniques, must be used throughout this work.

9.1 *Overview*:

9.1.1 Initially, reactors are filled with the ^{14}C-labeled polymer and fresh and decomposed refuse. Monitor reactors for gas volume and composition (CH_4, $^{14}CH_4$, CO_2, $^{14}CO_2$) as well as the presence of radiolabel in the leachate (^{14}C-organics, $^{14}CO_2$).

Also monitor the leachate pH and chemical oxygen demand. Analyze the gas collected in gas bags every two to four weeks, and analyze the leachate at the same frequency. A more frequent monitoring frequency will likely be necessary early in the experiment when gas production is high and leachate composition is less stable. Initially, gas production may be so high as to require weekly or even more frequent gas analysis.

9.1.2 At the completion of the refuse decomposition cycle, dismantle the reactors and remove the refuse solids so they can be analyzed for residual radiolabel. Dry the solids, grind them in a wiley mill to pass through a 0.5-mm screen and then analyze them for ^{14}C. This analysis is done by combustion of a solid sample and then trapping the evolved carbon as $^{14}CO_2$. Once data on the amount of residual radiolabel is available, calculate the fractions of the added radiolabel converted to $^{14}CH_4$ and $^{14}CO_2$, solubilized, and remaining with the refuse solids. The material remaining with the refuse solids may be either undegraded material, cell mass or some other transformation product. Detailed protocols for each aspect of reactor loading, monitoring, takedown and final analysis are presented in 9.2-9.10.

9.1.3 Operate reactors to accelerate refuse decomposition (*1*) by the addition of a seed of well-decomposed refuse to eliminate the lag period or acid phase of decomposition, (*2*) by the neutralization and recirculation of leachate through the reactors and (*3*) by the incubation of the reactors at 37°C, the optimal temperature for mesophilic refuse decomposition. These steps make it possible to simulate complete refuse stabilization, as evidenced by little or no measurable methane production, in six months. Seeding the reactors and operating them at high moisture content and neutral pH without leachate recirculation is expected to lead to similar results.

9.2 *Reactor Loading*:

9.2.1 Place a layer of fiberglass mesh on the bottom of the reactor to prevent large solids from plugging the reactor outlet.

9.2.2 Mix seed and fresh shredded refuse in a desired ratio of 30/70 by volume, which may be approximately 50/50 by dry weight. One thousand grams of total mixture should prove sufficient to fill a 2-L reactor. The effectiveness of the seed in initiating methane production from refuse should be verified in preliminary work. Add sufficient water so that the refuse may be compacted.

9.2.3 Add the refuse mixture to the reactor in approximately 75-mm lifts and compact the mixture after each addition.

9.2.4 After the reactor is half full, add radiolabeled material to the center of the reactor. Continue filling the reactor with the rest of the refuse.

9.2.5 Add a layer of cheesecloth and 454 g of 3-mm glass beads over the refuse. The cheesecloth and glass beads will distribute leachate recycled to the top of the reactor.

9.2.6 Close the reactor and connect a gas bag to the reactor outlet.

9.2.7 Leak-test all reactor joints to ensure that the system is gas tight by drawing a vacuum on one section of the reactor at a time and verifying that it holds a vacuum.

9.2.8 Add water to the leachate vessel and pump it over the refuse. Drain the leachate from the refuse and check the volume remaining. Adjust, if necessary, to achieve a final leachate volume of at least 500 mL (based on a 2-L reactor).

9.3 *Leachate Recycle and Neutralization*:

9.3.1 Check the pH of the leachate daily and adjust with 2 *M* NaOH/HCL to achieve the desired pH of 7.0 ± 0.3. Once the leachate exhibits this pH consistently without acid or base addition, change to a weekly monitoring of pH.

9.3.2 Recycle leachate five to six times a week.

9.4 *Gas Composition*—Methane and carbon dioxide are typically measured by using a gas chromatograph (GC) equipped with a thermal conductivity detector. Concentrations of 1 to 50 % by volume can be expected. Helium is typically used as the carrier gas. Calibrate the GC by using a series of external standards with differing concentrations of CH_4 and CO_2.

9.5 *Gas Trapping for Measurement of* $^{14}CH_4$ *and* $^{14}CO_2$:

9.5.1 Assemble the gas trapping system using four 20-mL serum bottles filled with 15 mL of 2 *M* NaOH to act as CO_2 traps. Place two traps before the combustion furnace and two after the furnace (Fig. 1). When inserting needles in the traps, be certain that the incoming needle extends to the bottom of the trap and the exhaust needle is in the headspace of the trap.

9.5.2 Inject a total of 400 mL of sample through the traps in 50-mL increments. Feed the gas into the gas trapping system at 20 mL/min by using a syringe pump. Use O_2 as the carrier gas at 30 mL/min. Supply O_2 in excess of the stoichiometric amount required to oxidize the CH_4 in the sample.

9.5.3 After the injections are complete, cover the injection port with any tape that fits tightly over the port and let the carrier gas continue to flow through the system for at least 30 min. Then add 1 mL from each trap to scintillation cocktail. Before scintillation counting, incubate samples in a refrigerator for at least 12 h to reduce chemiluminescence.

9.6 *Gas Volume Determination*:

9.6.1 With reference to Fig. 2, evacuate the stainless steel cylinder with a vacuum pump to 100 to 200 mbars while keeping the valve between the cylinder and gas sample closed. Vent the pump outlet to a fume hood. Record the initial pressure.

9.6.2 Connect the gas bag to the luer fitting and open valve 2. Allow gas to flow from the gas bag until the pressure reaches a value greater than 950 mbars. Close valve 2 and record the pressure. Repeat this procedure until the gas bag is evacuated. If the bag is evacuated before reaching 950 mbars, then close valve 2 and record the pressure.

9.6.3 After all the gas has been evacuated from a bag, open both valves and let the cylinder achieve room pressure. Record this pressure as atmospheric pressure.

9.6.4 Calculate the gas bag volume as follows:

$$Vs = \frac{Vc \times \Sigma(Pf - Pi)}{Pa} \quad (1)$$

where:

Vs = volume of sample, mL,
Vc = volume of the cylinder, mL,
Pf = final pressure of cylinder, mmHg,
Pi = initial pressure of cylinder, mmHg, and
Pa = atmospheric pressure.