



Standard Test Method for Volatile Organic Compound (VOC) Solvents Absorbed/ Adsorbed By Simulated Soil Impacted by Pesticide Emulsifiable Concentrate (EC) Applications¹

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1. Scope

1.1 This test method simulates the application of an emulsion of a pesticide emulsifiable concentrate (EC) to soil with high organic matter (corn cob granules) and to soil with high inorganic matter (clay granules) and determines the amount of solvent retained by the granules, and withheld from the atmosphere, before and after exposure to 40°C in a vented oven. The granules simulate two extremes of soil composition, and the 40°C exposure simulates high temperature weathering. Solvent loss from organic substrates other than corn cob may also be determined by repeating the 40°C exposure tests with the chosen substrate replacing corn cob. The results with corn cob, however, are a reference that must be reported with the alternate substrate results. The difference in solvent content of the granules before and after weathering is an indication of the emission of the solvent from soil impacted by emulsions or solutions during pesticide applications using common practices such as spraying and drip irrigating. Analysis of the granules for solvent content is by high pressure liquid chromatography (HPLC), gas chromatography (GC), or other methods tested and proven to be accurate and reproducible.

NOTE 1—Since it evaluates soil surface sorption, this test method will underestimate soil sorption from pesticide applications made below the soil surface. Sub-soil surface treatments may include, but are not limited to, mechanical soil injection and soil incorporation applications. In these cases, the increased depth of the sub-soil treatments reduce the soil surface exposure and facilitate increased levels of soil sorption.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appro-*

priate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 Other Standards:²

40 CFR 51.100(s) Protection of Environment—Requirements for Preparation, Adoption, and Submittal of Implementation Plans—Definitions

3. Terminology

3.1 Definitions:

3.1.1 *absorb*, *v*—a process in which one material (the absorbent) takes in, and retains, through its pores and interstices the molecules of another material (the adsorbate).

3.1.2 *adsorb*, *v*—a process in which one material (the adsorbent) attracts to, and retains on, its surface the molecules of another material (the adsorbate).

3.1.3 *emulsifiable concentrate*, *n*—a single-phase liquid system having the property of forming an emulsion when mixed with water.

3.1.4 *emulsifying agent*, *n*—a surfactant that promotes the suspension of one liquid in another.

3.1.5 *gas or liquid chromatography*, *n*—a process in which a chemical mixture carried by a mobile liquid or gas is separated into components as a result of different affinities of the components for the liquid or gas and the adsorbing medium through which they pass.

3.1.6 *inorganic matter*, *n*—substances of mineral origin that are not characterized by primarily carbon-based structures.

3.1.7 *organic matter*, *n*—in soil, organic matter consists of plant and animal material that is in the process of decomposing.

3.1.8 *tropospheric ozone*, *n*—an air pollutant formed by the sunlight catalyzed reaction between hydrocarbons and nitrogen

¹ This test method is under the jurisdiction of ASTM Committee E35 on Pesticides, Antimicrobials, and Alternative Control Agents and is the direct responsibility of Subcommittee E35.22 on Pesticide Formulations and Delivery Systems.

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² Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, <http://www.access.gpo.gov>.

oxides present in the troposphere, the layer of the atmosphere closest to the earth's surface.

3.1.9 *volatile organic compound (VOC), n*— any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions; excluded is a list of organic compounds which have been determined to have negligible photochemical reactivity (40 CFR 51.100(s)).

3.1.10 *volatilize, v*—to pass off as vapor; to evaporate.

4. Summary of Test Method

4.1 A pesticide EC (emulsifiable concentrate) is simulated with a concentrate consisting only of solvent plus emulsifying agent(s). The concentrate is then mixed with water, and the emulsion is applied to corn cob granules (organic substrate) and montmorillonite clay granules (inorganic substrate), which absorb/adsorb the liquid.

4.2 Other organic substrates, like corn stover, straw, or sphagnum peat, for example, may simulate the harvest debris from some crops better than corn cob, and the test method can be used with any of this type substrate replacing corn cob. Care must be taken to select a substrate appropriate for the crop of concern, and the results with corn cob are a reference that must be reported with the alternate substrate results. The treated granules are placed in a vented 40°C oven in uncapped bottles. The uncapped bottles allow for loss of the solvent by volatilization. Each bottle is left in the oven for a different, and ever increasing, time period. The time period for the first bottle may be as little as two hours, and that for the last bottle may be as much as one-hundred twenty hours or longer. After the 40°C exposure, the granules are analyzed to determine the amount of solvent still retained. Successive time periods continue until the amount of solvent found in two or more successive samples indicates more exposure time is not expected to cause significantly more loss of solvent. Analysis is by high pressure liquid chromatography (HPLC), gas chromatography (GC), or other methods tested and proven to give accurate and reproducible results.

5. Significance and Use

5.1 This test method is designed specifically for emulsions of pesticide emulsifiable concentrates.

5.2 This test method provides information on the absorption/adsorption of solvents by simulated organic soil and inorganic soil impacted by pesticide EC emulsion applications.

5.3 The amount of solvent lost by volatilization at 40°C as determined by this method is an indirect measure of the atmospheric availability of the solvent to potentially react with nitrogen oxides to form tropospheric ozone, a major air pollutant.

6. Apparatus

6.1 *Balance*, sensitivity of 0.01 g.

6.2 *Roller System*, two or more rollers with a drive bed, capable of rotating a glass bottle or jar, about 1 to 4 L in size, at 20 to 60 r/min.

6.3 *Glass bottle or jar*, round, with screw-thread cap, for use with roller system. Typical size is 1 to 4 L.

6.4 *Oven*, vented, mechanical convection, $40 \pm 2^\circ\text{C}$, 2.0 ft³ minimum inside capacity, 50 to 90 air exchanges per hour.

6.5 *125-mL laboratory media bottles*, glass, round, outside diameter about 55 mm, height about 123 mm, inside diameter opening about 30 mm, with screw-thread caps. An example is Wheaton brand, available from many laboratory supply companies.

6.6 Apparatus required by the analytical test method.

7. Reagents and Materials

7.1 Corn cob granules, 20/40 Mesh

7.2 Montmorillonite clay granules, LVM, 12/24 Mesh.

7.3 Solvent to be tested.

7.4 Emulsifying agent(s) suitable for emulsifying the solvent.

7.5 Reagents and materials required by the analytical test method.

8. Hazards

8.1 Before testing, read the precautionary statements on product labels and the Material Safety Data Sheets (MSDS). Take proper precautions to prevent skin contact and inhalation of fumes or dust. Take care to prevent contamination of the surrounding area. Always wear the appropriate safety equipment and, where indicated, wear respiratory devices approved by the National Institute of Occupational Safety and Health (NIOSH) for the product being tested.

8.2 Store, handle, and dispose of test materials with consideration for health and environmental safety, and in accordance with federal, state, and local regulations.

9. Sampling, Test Specimens, and Test Units

9.1 The uniform mixing of the roller system procedure ensures any size sample taken from the roller system jar is a representative sample. Do not use riffing to reduce a gross sample of the treated granules to a representative, suitable size. Significant volatilization of the solvent may occur during riffing or any other time the granules are not in a sealed container.

10. Preparation of Apparatus

10.1 For all apparatus, see the manufacturers' instructions for proper operation and maintenance.

11. Calibration and Standardization

11.1 See the analytical test method to be used for determining solvent content for information relative to calibration and adjustment of the apparatus necessary for the use of the method.

11.2 See the analytical test method for the standardization and use of reference standards and blanks used in the method.

12. Procedure

12.1 Prepare an emulsifiable concentrate consisting only of solvent plus emulsifying agent(s). A typical formula is 90 to 92 % solvent and 8 to 10 % emulsifying agent(s). Check the emulsion performance by adding 1 part concentrate to 14 parts water. Stir the mixture to form the emulsion. The emulsion should form easily, remain free of separation for 15 min, and re-emulsify easily after sitting 24 h. If the concentrate does not meet these performance limits, reformulate using a different emulsifying agent(s). Keep the concentrate and the emulsion in closed containers, regardless of the ambient temperature, to prevent loss of solvent by volatilization. Open the containers only for the time needed to perform a necessary task.

12.2 Analyze the concentrate for weight % solvent, using the same analytical method to be used for the treated granules. Repeat the analysis. The two analyses must not differ more than 4 % from each other. Use the average to calculate the make-up of the emulsion to be used for treating the granules.

12.3 Prepare one batch of emulsion treated corn cob granules and one batch of emulsion treated clay granules as described below. These are the primary sampling units. Test unit samples are sub-units taken from these primary units.

12.4 Keep all treated granules in closed containers, regardless of the ambient temperature, to prevent loss of solvent by volatilization. Open the containers only for the time needed to perform a necessary task.

12.5 Typically, the desired weight % solvent in granules for analysis by HPLC or GC is about 1 % . A suggested protocol for the preparation of granules with 1 % solvent is as follows: Prepare a concentrate of 90 % solvent plus 10 % surfactant(s). Add 1.1 parts concentrate to 14 parts water. Add the resulting emulsion to 85 parts granules and mix to uniformity. Determine the initial solvent content of the granules by extracting a sample with a suitable analytical solvent followed by analysis of the extract. The weight of the sample, or test unit, for 40°C exposure and subsequent analysis is the weight determined to be nominal for the analytical method.

12.6 Begin preparation of the two batches of treated granules by adding untreated granules to the glass bottle or jar to be rotated on the roller system. The granules should fill one-fourth to one-half the container for the best mixing by rotation to occur.

12.7 Add the emulsion to the granules in three equal increments using enough total emulsion to give good distribution of the liquid but not enough to wet the granules to the point of significantly changing their flow properties. Use a transfer pipette to add the emulsion to the inside wall of the container while the container is being tilted and rotated by hand. The goal is to spread the liquid in a thin film on the wall so that the liquid does not contact the granules in a concentrated area as would happen by just pouring the liquid on the granules. Concentrating the area where the liquid contacts the granules may cause clumps, which then require extra mixing care to re-fragment .

12.8 Add the first emulsion increment, promptly cap the container, and place it on the roller system at, typically, 30 to 50 r/min for a good cascading motion that gives good mixing

of the granules inside. Rotate 10 min. Repeat the increment additions of emulsion and 10 min rotating two more times.

12.9 Use an analytical method tested and proven to give accurate and reproducible results. HPLC and GC methods have been used successfully.

12.10 Determine by trial and error the number of successive time periods needed for tracking the loss of solvent from the granules by volatilization at 40°C to a plateau indicating further loss is not expected to be significant. A minimum of five successive time periods is needed to conclude the plateau occurs; two of those periods must be 0 h and 72 h. Tracking is completed when the results from any two of three successive time periods do not differ from each other by more than the accuracy of the test method. See 15.2 for repeatability and reproducibility standard deviation and the 95 % repeatability and reproducibility limits on the difference between test results.

In the rare event it is concluded that a plateau for loss by vaporization will not be seen, the half-life for biodegradation of the solvent in soil can be used as a second tier end-point. Stop the testing after exposure time at 40°C equals 3× the biodegradation half-life. The determination of soil biodegradation half-life, itself, is beyond the scope of this test.

12.11 A suggested sequence of successive time periods at 40°C for starting trial and error tests is: 0 h, 8 h, 24 h, 48 h, 72 h, 96 h, and 120 h.

12.12 A suggested testing protocol is as follows: Prepare three sets of seven 125-mL media bottles containing the treated granules. Trial and error results may reduce or increase the number of samples actually needed.

12.13 Weigh the empty bottle and cap to the nearest 0.01 g. Add a test unit (nominal weight) of granules to the bottle. Typically, the nominal weight of granules for HPLC analysis is 5 g, and the nominal weight for GC analysis is 5 to 20 g. Use the nominal weight specified by the analytical method for all 40°C exposures and solvent extractions.

12.14 Weigh the bottle and granules and cap to the nearest 0.01 g. Determine the exact weight of the granules to the nearest 0.01 g.

12.15 For each set of seven bottles, label bottle #1 for Wt % Solvent after 0 h @ 40°C, label bottle #2, #3, #4, #5, #6, and #7 for Wt % Solvent after 8, 24, 48, 72, 96, and 120 h @ 40°C, respectively.

12.16 For each set of seven bottles, remove the caps from bottles #2 through #7 and place the uncapped bottles in the 40°C oven for the specified time periods. Remove each bottle from the oven at the end of its time period and promptly replace the cap.

12.17 Determine the Wt % Solvent in each of the first 5 test units of the first set of bottles. If the results do not show a plateau, analyze test units 6 and 7. If the plateau is still not evident, continue trial and error testing with longer time intervals.

12.18 Determine the Wt % Solvent of the test units of the second set of bottles, using only the time periods for 40°C

exposure determined to be appropriate by the trial and error results from the first set. If the results of any single time period from sets one and two differ from each other by more than 4 %, repeat the test for that time period using a test unit from set three.

13. Calculation or Interpretation of Results

13.1 Calculate the Wt % Solvent of each test unit using the formula shown in the analytical method used for the analysis. Use the weight of the granules as determined in 12.4, that is, the pre-40°C exposure weight, for the calculations.

14. Report

14.1 Report the name of the test solvent and what is known of its purity and source.

14.2 Provide the formula for the emulsifiable concentrate, identifying the emulsifying agent(s) by trade name.

14.3 Report the trade name and mesh size of the corn cob granules. Report the trade name and mesh size of the montmorillonite clay granules.

14.4 Identify the analytical test method used for analysis of the emulsifiable concentrate and treated granules. Report the title of the method, the source, and any identifying numbers or codes attached to the method.

14.5 Report the individual test results, and their averages, for 0 h, 72 h, and a minimum of three other time periods. Report the results from at least two sets of data, which can not differ from each other by more than 4 %. Results from three

sets of data can not differ from the average of the three by more than 4 %. **Table 1** and **Table 2** are guides for reporting.

15. Precision and Bias

15.1 This test method does not contain pass/fail limits. The data and conclusions are intended for comparative information.

15.2 The repeatability standard deviation and 95 % repeatability limits on the difference between two test results are shown in the research report.³ The reproducibility standard deviation and 95 % reproducibility limits on the difference between two test results are shown in the research report.

16. Keywords

16.1 air pollutant; atmospheric availability; inorganic soil; organic soil; pesticide solvent emissions; simulated soil; solvent retention by soil; tropospheric ozone; volatile organic compound (VOC)

³ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E35-1002.

TABLE 1 Weight % Solvent in Corn Cob Granules After 40°C Exposure

Test Unit, g	Hours at 40°C ^A	Set 1	Set 2	Set 3	Average
	0 (mandatory)				
	8				
	24				
	48				
	72				
	(mandatory)				

^A Five or more time periods.

TABLE 2 Weight % Solvent in Clay Granules After 40°C Exposure

Test Unit, g	Hours at 40°C ^A	Set 1	Set 2	Set 3	Average
	0 (mandatory)				
	8				
	24				
	48				
	72				
	(mandatory)				

^A Five or more time periods.

ANNEX

(Mandatory Information)

A1. TRADE NAMES OF MATERIALS

A1.1 Emulsifying agents are marketed by the chemical class of the surface active ingredient of the product. But most products also contain unidentified impurities and solvents which are manufacturer dependent. The unknown ingredients may cause differences in the analytical results of users of this test method who use emulsifying agents from different manufacturers. Identifying the emulsifying agents by trade name is required until reproducibility data shows the requirement can be deleted.

A1.2 The absorption, adsorption, and solvent retention properties of corn cob granules and montmorillonite clay

granules from different manufacturers may vary enough to affect test method results. Identifying the materials by trade name is required until reproducibility data shows the requirement can be deleted.

A1.3 Solvents used in pesticide EC formulas are usually industrial grade. Those made by different manufacturers may have different impurities which have different effects on test method results. Identifying the source of the solvent by trade name is required until reproducibility data shows the requirement can be deleted.

APPENDIX

(Nonmandatory Information)

X1. REASON FOR THE DEVELOPMENT OF THIS TEST METHOD

X1.1 The Federal Clean Air Act sets limits on the amount of volatile organic compound (VOC) that can be released into the atmosphere. The current test method used by the California Department of Pesticide Regulation (CDPR) for assessing the potential amount of released VOC arising from the application of a pesticide emulsifiable concentrate (EC) uses a thermogravimetric analysis (TGA) test method. The test has flaws. First, the test sample in the TGA test is undiluted EC, but in actual applications the EC is diluted with water. Second, the TGA test ignores the hindering of emission that occurs when volatile

compounds of the applied dilution are absorbed/adsorbed by both soil and vegetation. Third, the TGA test temperatures, 115°C (239°F) and 55°C (131°F) may cause volatilization or decomposition that does not happen in actual pesticide usages because application temperatures rarely exceed 40°C (104°F).

X1.2 This test method looks for the amount of solvent in a pesticide EC application that is not available for volatilization into the atmosphere because it is tied up in the soil.

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