

Estimation of Volatile Emission Potential of Pesticides by Thermogravimetry

I. OVERVIEW

The potential for solid or liquid pesticides to emit volatile organic compounds (VOCs) is estimated by thermogravimetric analysis (TGA). Pesticide samples are heated in an environmentally controlled chamber and then held isothermally until the rate of sample mass loss drops below a defined threshold. The mean of three replicate measurements is used to estimate a pesticide product's emission potential (EP) as follows:

$$\begin{aligned} \text{EP} = & \text{mean (\% TGA sample mass loss)} \\ & - (\text{product \% water}) \\ & - (\text{product \% exempt compounds}) \end{aligned}$$

where a product's water and exempt compound percentages can be obtained from a statement of formula. The current list of exempt compounds, which is occasionally revised, can be found in 40CFR 51.100(s).

The default test conditions utilize a final holding temperature of 115 °C to facilitate volatilization of water contained in a pesticide formulation. The TGA must be conducted using the 115 °C final holding temperature unless product constituents are thermally labile. An alternate test condition that utilizes a final holding temperature of 55 °C is used when

- there is known evidence of a product's thermal lability based on well-established constituent properties. Supporting documentation must be submitted to DPR to demonstrate this is the case.
- a product fails to reach a stable endpoint when analyzed at 115 °C, or when there is a marked discrepancy between the results from runs at 115 °C and at 55 °C that can be attributed to instability of the constituents. In either situation, both the 115 °C and the 55 °C thermograms must be submitted to DPR.

II. PROCEDURE

A. *Equipment/Materials*

(1) *Thermogravimetric analyzer.* — Any commercially available TGA consisting of a heating unit and an accurate microbalance housed in an enclosed environmental chamber meeting the following criteria will be adequate for this test procedure:

- (a) the TGA balance must be capable of accurately weighing to 10 µg;
- (b) temperature capabilities must span the 35 °C to 115 °C range,
- (c) the oven must be capable of a controlled heating rate of 5 °C per minute, and
- (d) the TGA must include the ability to print a thermogram of mass loss versus time.

Volatility is estimated from sample mass loss measured in a computer-controlled oven chamber using a recording microbalance to determine the endpoint.

(2) *Gas flow controller.* — For control of inert N₂ purge gas; adjustable from 50 to 80 mL per minute. A flow rate of 60 to 70 mL/min. is used for these analyses.

(3) *Specimen holder.* — Disposable aluminum sample pans, such as those used in differential scanning calorimetry (DSC) instruments, are used to hold the sample during testing (Perkin-Elmer 0219-0041; TA Instruments 900786-901; or equivalent).

(4) *Specimen vials and transfer materials.* — Suggested: small amber glass bottle with phenolic Teflon-lined cap; stainless steel needle-nose forceps; spatulas; Xacto™ knife, scalpel or single-edged razor blades; vinyl electrical tape; weighing boats.

(5) *Purge gas.* — Compressed dry nitrogen, ≥99.9% purity. Flow rate to be set at 60-70 mL/min.

B. Preparation of Specimen Holders

Sample pans are conditioned at 125 °C for one hour and stored in a desiccator prior to use.

C. Sample Preparation

The pesticide sample must be withdrawn from a commercial container of the product as described below. The original sampling may be done wherever it is most convenient -- at the manufacturing facility, at a distribution point, or at the lab. Gently mix the contents of the pesticide container to obtain a representative sample for this test. Immediately transfer enough pesticide to underfill a small labeled amber glass bottle. Seal with a Teflon-lined cap and secure with vinyl electrical tape. The samples for TGA analysis will be withdrawn as needed from this bottle.

D. Calibration of Thermogravimetric Analyzer

Calibrate the TG Analyzer according to the instrument manual and the guidelines listed below before initial pesticide analysis is undertaken. Use a nitrogen purge flow rate of 60 to 70 mL per minute. Recalibrate the TGA as necessary during the course of analyses if significant parameters, such as gas flow rate, change.

(1) *Mass calibration.* Calibrate the TG Analyzer balance with a 10-mg Class I certified reference weight according to the manufacturer's instructions.

(2) *Two-point temperature calibration.* Calibrate the TG analyzer temperature sensor at 2 different temperatures. For the initial point, calibrate the instrument temperature sensor at or near room temperature according to the manufacturer's instructions. Calibrate the second point at a temperature near, but greater than, 115 °C . One approach is to calibrate with reference to an alumel Curie point standard with a magnetic transition of 163 °C according to §8.0 of the ASTM method E 1582–93, "Standard Practice for Calibration of Temperature Scale for Thermogravimetry" (ASTM, 1993).

E. Pesticide Sample Analysis for Estimation of Potential Volatility

The TGA procedure described here applies to both the 115 °C and 55 °C regimens defined above; the endpoints of the analyses depend on the final temperature as noted. Choice of temperature regimen is determined by the criteria previously discussed.

Equilibrate pesticide samples in their sealed containers to room temperature prior to testing. Dry formulations should be conditioned at room temperature in a desiccator over a drying agent. Place the pre-dried sample pan onto the TGA stirrup, close the furnace enclosure, heat to a starting temperature of 35 °C, and tare off the weight of the empty pan.

For liquids, immediately before sampling gently agitate the contents of the sample container until mixed; it is critical that the contents are homogeneous when the TGA aliquot is withdrawn. Weigh a 10-mg ($\pm 10\%$) sample into the aluminum sample pan. The beginning sample mass should be recorded as soon as the mass reaches a stable maximum. Some formulations contain highly volatile components requiring a minimal time delay between sample loading and recording of the sample mass.

For solid formulations in which the individual pieces are large (e.g. pellets), they must be cut up using a razor blade, sharp knife or scalpel. It is important to obtain a representative sampling of large pellets since they tend to be less homogeneous.

Document any additions or special procedures used in sample preparation or handling. Submit this information on the TGA data submission form.

(1) Analysis at 115 °C. — The sample is heated from 35 °C to 115 °C at a rate of 5 °C per minute and is then held isothermally until the mass-loss rate has **stabilized at 0.5% or less over a five-minute period; the sample is then held at 115 °C for an additional 15 minutes. VOC emission potential uncorrected for water content is defined as the total percentage mass loss from the pesticide at the end of this 15-minute period. If a product fails to attain the prescribed mass-loss rate after 80 minutes at 115 °C, the pesticide may contain an unstable component and should be retested at 55 °C.**

(2) Analysis at 55 °C. — The sample is heated from 35 °C to 55 °C at a rate of 5 °C per minute and is then held isothermally for 11 hours. Uncorrected VOC emission potential is defined as the total percentage mass loss **at the end of the 11-hour period.**

III. REPORTING REQUIREMENTS

A. TGA Results

Fill out and submit the TGA data submission form along with copies of the thermograms from all pesticide analyses. If the TGA was performed using the 55 °C regime because of observed thermal instability in the 115 °C regime, remember to also include the 115 °C thermograms along with the 55 °C thermograms.

B. Correction for Water and Exempt Compounds

The VOC emission potential should be corrected for water content of the pesticide product if that information is available. Water content will be determined based on submission of the product's statement of formula and/or statement(s) of formula for any inerts contained in the product. The statement(s) of formula should be submitted with the TGA submission form and thermograms. If statements of formula are not received, the "default" assumption will be that the product contains no water. The VOC emission potential should be similarly corrected for the presence of exempted compounds listed in 40CFR 51.100 (s). This correction will also be based on statement(s) of formula.