

VALENT USA CORPORATION
VALENT TECHNICAL CENTER
DUBLIN, CALIFORNIA

DETERMINATION OF FLUMIOXAZIN
RESIDUES IN SOIL
RESIDUE METHOD RM-30D

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INTRODUCTION

This method describes the procedure for determining residues of flumioxazin, [V-53482, 7-fluoro-6-((3,4,5,6-tetrahydro)phthalimido)-4-(2-propynyl)-1,4-benzoxazin-3(2H)-one] in soil. This method is based on a method developed by Sumitomo Chemical Co., Ltd¹. Briefly, the method involves extraction with acetone/0.1 N HCl (5/1, v/v), partition of the residues into dichloromethane, cleanup using Florisil column chromatography, and measurement by gas chromatography utilizing a nitrogen-specific flame-ionization detector.

This method was revised on February 7, 1991 to change the limit of detection from 0.01 ppm to 0.005 ppm, on March 6, 1991 to change the extraction solvent from acetone/H₂O (5/1) to acetone/0.1 N HCl (5/1), and on August 5, 1991 to change the GC column parameters. The method was further revised on September 27, 1995 to change the company header and to make other minor text changes.

REAGENTS

Acetone - Pesticide Quality or equivalent.

Dichloromethane - Pesticide Quality or equivalent.

Ethyl acetate - Pesticide Quality or equivalent.

Florisil - PR grade, U.S. Silica Co. or equivalent. Blend 2 parts 100-200 mesh and 3 parts 60-100 mesh and activate overnight at 130°C. Allow to cool overnight before using.

Hexane - Pesticide Quality or equivalent.

Hydrochloric Acid - 36.5 - 38.0%, Baker-Analyzed[®] Reagent, J.T. Baker or equivalent. Prepare a 0.1 N solution by carefully adding 40 mL of acid to 4 liters of deionized water.

Sodium chloride - Certified ACS grade or equivalent. Prepare a 5% (w/v) solution by dissolving 5 gram analytical grade crystals in 100 mL deionized water.

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REAGENTS (CONTINUED)

Sodium sulfate - Anhydrous, granular, reagent grade.

Water - Deionized.

REFERENCE STANDARDS

Flumioxazin - analytical standard of known purity, available from Valent U.S.A. Corporation. Prepare a stock solution containing 1.0 mg/mL of flumioxazin in acetone. Prepare a calibrating/fortifying solution by diluting this stock solution to 1.0 $\mu\text{g/mL}$ with acetone. Prepare a minimum of four linearity solutions ranging from 0.1 $\mu\text{g/mL}$ to 2.0 $\mu\text{g/mL}$ by diluting the stock solution with acetone. See Note 1. All solutions must be refrigerated when not in use.

EQUIPMENT

Eberbach Reciprocating Shaker or equivalent.

Liquid Chromatography Columns - 300 x 19 mm i.d. glass with Teflon[®] stopcock plugs.

Rotary Vacuum Evaporators - Büchi (Brinkman) equipped with a temperature controlled water bath or equivalent system.

Ultrasonic bath.

Büchner Funnels - 10 cm diameter.

Filter Flasks - 500 mL.

Filter Funnels - 10 cm diameter.

Round-bottom Flasks - 50 mL, 250 mL, and 500 mL capacity with 24/40 ground glass joints.

Filter paper - Whatman #1, 9 cm diameter.

Separatory Funnels - 500 mL equipped with Teflon[®] stopcocks.

Gas Chromatograph - Hewlett-Packard 5890A equipped with packed column injector port with megabore adaptor, a nitrogen-phosphorus flame ionization detector, autosampler, and integrator or equivalent system.

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ANALYTICAL PROCEDURES

Extraction

Thoroughly mix the sample. Transfer 10 grams (\pm 0.1 gram) to a 1 pint Mason jar. At this point, a control sample may be fortified for recovery purposes with an appropriate volume of the 1 $\mu\text{g}/\text{mL}$ fortifying solution of flumioxazin (e.g. 0.1 mL of this solution would fortify the sample with 0.01 ppm). See Note 2.

Add 50 mL of acetone/0.1 N HCl (5/1, v/v) and shake for 10 minutes. Allow to soak overnight at room temperature. Shake 10 minutes. Filter the supernatant through a Büchner funnel using Whatman #1 filter paper.

Return the filter cake to the Mason jar and repeat the extraction and filtration using another 50 mL acetone/ 0.1 N HCl (5/1, v/v). Rinse the filter cake with two 20-mL portions of extraction solvent.

Water/Dichloromethane Partition

Transfer the filtrate to a 500 mL separatory funnel and add 150 mL of 5% aqueous sodium chloride solution. Add 80 mL of dichloromethane to the separatory funnel in two portions, using each portion to rinse the filter flask. Shake for 1 minute.

Filter the dichloromethane extract through a 10 cm filter funnel containing approximately 50 grams of sodium sulfate (suspended on a plug of glass wool and freshly washed with 20 mL of dichloromethane) and collect the extract in a 500 mL round bottom flask.

Repeat the partition and filtration steps with an additional 60 mL portion of dichloromethane. Rinse the sodium sulfate cake with 20 mL of dichloromethane. Evaporate the combined dichloromethane extracts to dryness using a rotary vacuum evaporator equipped with a water bath set at $\leq 40^\circ\text{C}$. See Note 3.

Florisil Column Cleanup (See Note 4)

Place a glass wool plug at the bottom of a 300 mm x 19 mm i.d. glass chromatographic column. Close the column stopcock and add 40 mL hexane/ethyl acetate (2/1, v/v) to the column. Slowly add 15 grams of activated Florisil to the column while gently tapping the side of the column. Rinse the sides of the column with a small amount of hexane/ethyl acetate (2/1, v/v) (typically two or three 3 mL portions). Open the stopcock and allow the solvent to drain to the top of the packing.

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Redissolve the concentrated sample residue in 1 mL of ethyl acetate, dilute with 2 mL of hexane, and sonicate for at least 15 seconds. Transfer the extract to the top of the column. Rinse the round bottom flask with three 3-mL portions of hexane/ethyl acetate (2/1, v/v). Transfer each rinse to the column, allowing each 3-mL portion to drain to the top of the column before adding the next rinse.

Elute the column with an additional 28 mL of hexane/ethyl acetate (2/1, v/v) (total volume 40 mL). Discard this eluate. Place a 250 mL round bottom flask under the column and elute the flumioxazin with 70 mL of hexane/ethyl acetate (2/1, v/v).

Evaporate this eluate to dryness using a rotary vacuum evaporator equipped with a water bath set at $\leq 40^{\circ}\text{C}$. Transfer the residue to a 50 mL round bottom flask using three 5-mL portions of acetone (sonicate the flask for at least 15 seconds if necessary) and evaporate to dryness using a rotary vacuum evaporator equipped with a water bath set at $\leq 40^{\circ}\text{C}$. See Note 3.

MEASUREMENT

Redissolve the residue in 0.5 mL acetone. A sample may be dissolved in a larger volume of acetone if the flumioxazin concentration is expected to exceed the concentration of the highest linearity standard. Quickly transfer the sample to an autosampler vial using a Pasteur pipet and seal immediately to minimize evaporation losses.

Load the autosampler with the sample and reference standard vials and analyze using the following parameters:

Column: 15 M x 0.53 mm ID, DB-17 (50% phenyl-methyl silicone megabore column
1.0 μm film, J & W Scientific Cat # 125-1712 or equivalent.

Column Temperature Program:

Initial Temperature: 250°C
Initial Hold Time: 1 minute
Program Rate: $20^{\circ}\text{C}/\text{minute}$
Final Column Temperature: 280°C
Final Hold Time: 8 minutes

Carrier Gas Flow Rate: 10 mL/min (He)
Auxiliary Gas Flow Rate: 25 mL/min (He)
Hydrogen Flow Rate: 3.5 mL/min
Air Flow Rate: 110 mL/min
Injector Temperature: 275°C
Detector Temperature: 300°C
Injection volume: 1 μl
Retention Time: 5.7 min. (See Figure 1)

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The parameters shown are given only as a guide. They may be modified as needed to optimize the chromatography or to resolve matrix interferences. Each set of chromatograms must be clearly labelled with the GC parameters used. The recommended sequence of analysis of samples and standards is: conditioning sample, calibrating standard, sample, calibrating standard, sample, calibrating standard, sample, etc. This sequence may be modified if the reproducibility requirement is met. See Note 5.

CALCULATION

Use the following formula to calculate the amount of flumioxazin present in the samples:

$$\text{ppm flumioxazin} = \frac{B \times C \times V \times DF}{A \times W}$$

Where

- B = integration counts for flumioxazin in the sample.
- C = concentration of flumioxazin in the calibrating standard (1.0 $\mu\text{g/mL}$).
- V = final volume of the sample extract (0.5 mL).
- DF = dilution factor, used if the sample extract is diluted prior to analysis.
- A = mean integration counts for the flumioxazin calibrating standards.
- W = sample weight (10 grams).

LIMITS OF DETECTION AND QUANTITATION

The limit of detection for flumioxazin in soil analyzed by this method is 0.005 ppm. The validated limit of quantitation for flumioxazin in soil analyzed by this method is 0.01 ppm.

NOTES

1. At Valent, the linearity of the gas chromatographic system must be verified each day that samples are analyzed (Valent SOP #VR-007). Linearity is determined by analyzing at least four linearity standards ranging in concentration from 0.1 $\mu\text{g/mL}$ to 2.0 $\mu\text{g/mL}$. The mean of the response factors (response equivalent to 1 $\mu\text{g/mL}$) should have a coefficient of variation of $\pm 10\%$ or less. Deviations to this requirement require the approval of the chemist responsible for the analysis.


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2. At Valent, at least one fortified control sample must be analyzed concurrently with each set of samples. The level of fortification is generally 0.01 ppm (the LOQ of the method) and/or 0.05 ppm. These fortifications are made by adding 0.1 mL and 0.5 mL, respectively, of the 1.0 $\mu\text{g}/\text{mL}$ fortifying solution to a 10 gram sample. Method recovery must be between 70% to 120% to be acceptable unless approved by the chemist responsible for the analysis. Analysis of fortified control samples may not be required at other facilities.
3. Samples must be removed from the rotary evaporator immediately after the solvent has evaporated to avoid loss of flumioxazin.
4. Each batch of Florisil must be checked for recovery of flumioxazin as follows: Transfer 1.0 mL of the 1.0 $\mu\text{g}/\text{mL}$ flumioxazin fortifying solution to a 50 mL round-bottom flask and evaporate to dryness using a rotary-evaporator and water bath set to $<40^\circ\text{C}$. Transfer the residue to a Florisil column and elute the flumioxazin as described under Florisil Column Cleanup. Evaporate the eluate to dryness, add 1.0 mL of acetone and swirl to completely dissolve the residue. Analyzed this eluant and the 1.0 $\mu\text{g}/\text{mL}$ calibrating standard as described under Measurement. If the flumioxazin peak for the eluant is less than 90% of the calibrating standard, then the elution profile of flumioxazin must be determined.
5. At Valent, the reproducibility of an analytical run is determined by calculating the CV from the peak units obtained for the calibrating standards analyzed during the run. For a run to be acceptable, this CV must be 10% or less unless approved by the chemist responsible for the analysis (Valent SOP #VR-013).

REFERENCE

1. Ohnishi, J., Hirota, M. and Yamada, H., Report No. ER-MT-8939, "Residue Analytical Method for S-53482 in Soil," November 24, 1989.

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