

(+)-ethyl 2-[4-[(6-chloro-2-benzoxazolyl)oxy] phenoxy]propanoate, HOE 33171
Acclaim, Furore Whip

CAS 82110-72-3

I American Hoechst Corp Route 202-206 North, Somerville NJ 08876 -
Method submitted with Pesticide Petition 6F3316 Attached as Method I

Residues of fenoxaprop-ethyl and its major metabolites are extracted from various matrices e g soybean seed and rice grain, and converted to the degradation product HOE 054014 by refluxing in acetonitrile-HCl for 6 h Coextracted substances are eluted with hexane from an Extrelut column HOE 054014 is derivatized with acetic anhydride to HOE 083312 which is cleaned up on a C-18 Sep-Pak cartridge and then on a minicolumn of silica gel Fenoxaprop-ethyl and its metabolites are determined as HOE 083312 by GC with electron capture detection on a column of 3% SP-2100 on 100/120 mesh Supelcoport

In a method tryout EPA obtained recoveries of fenoxaprop-ethyl that ranged from 68 to 88% for triplicate soybean samples fortified at the 0.05 and 0.10 ppm levels Recoveries of fenoxaprop and HOE 054014 ranged from 70 to 86% and from 80 to 90% respectively, for triplicate soybean samples fortified at the same levels

Product application soybeans

Detection limit 0.05 ppm

Gas Chromatographic Determination of Residues of
Fenoxaprop-Ethyl and Its Major Metabolites in Various Matrices

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(Method AL 48/86 November 12 1986, developed by Hoechst
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Principle

Residues of fenoxaprop-ethyl and its major metabolites are extracted from various matrices by refluxing in acetonitrile-concentrated HCl (90+10) for 6 h. During this process fenoxaprop-ethyl and fenoxaprop (HOE 053022) 2-[4-(6-chloro-2-benzoxazolyl)phenoxy]propanoic acid are converted to HOE 054014 6-chloro-2,3-dihydrobenzoxazol-2-one.

The reflux mixture is diluted with water to bring the acetonitrile concentration to 50%. Any undissolved material is removed by filtration. An aliquot of the filtrate is transferred to an Extrelut column from which coextracted substances are eluted with hexane. The hydrolysis product from the reflux HOE 054014 is subsequently eluted with ethyl ether-hexane (20+80).

The eluate containing HOE 054014 is concentrated to near dryness and any remaining hexane is removed by adding small portions of ethyl acetate and evaporating to 2 mL after each addition. An aliquot of the ethyl acetate solution is then evaporated to dryness and the HOE 054014 is derivatized over 3 h at 130°C by using acetic anhydride with pyridine as the catalyst.

The derivative HOE 083312 3-acetyl-6-chloro-2,3-dihydrobenzoxazol-2-one is cleaned up on a C-18 Sep-Pak cartridge followed by a minicolumn of silica gel.

Fenoxaprop-ethyl and its metabolites are determined as HOE 083312 by gas chromatography with electron capture detection on a column of 3% SP-2100 on 100/120 mesh Supelcoport. Total residue is expressed as fenoxaprop-ethyl equivalents.

The structures of fenoxaprop HOE 054014 and HOE 083312 are shown in Figures 1-3.

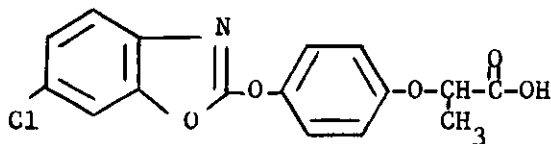


Figure 1 Structure of fenoxaprop

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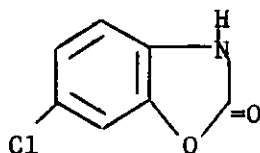


Figure 2 Structure of HOE 054014

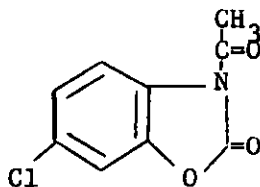


Figure 3 Structure of HOE 083312

Apparatus

- (a) High-speed blender - Waring Model 31 BL 46 with 1 qt containers
- (b) Balances - Mettler Model PC 2000 or equivalent (for sample preparation), Mettler Model AE 160 or equivalent (for standard preparation)
- (c) Microliter syringes - 100 250 and 500 μ L (Hamilton or equivalent)
- (d) Polytron homogenizer - Brinkmann PT 10/35 with PTA 20 TSM generator
- (e) Round-bottom flasks - 500 mL with F 29/42 ground glass joint (Ace Scientific 6887-407) 500 mL with F 24/40 ground glass joint (Fisher Scientific 10-0676)
- (f) Reflux condenser - High-efficiency 12' equipped with F 29/42 ground glass joint (Ace Scientific 5955-34)
- (g) Heating mantles - Glas-Col, 500 mL (Fisher Scientific 11-472-10F)
- (h) Glass funnels - Pyrex 10 cm diameter (Fisher Scientific 10-329 D)
- (i) Fluted filter paper - 24 cm fast (S&S 588)
- (j) Volumetric pipets - Glass 1 10 and 20 mL
- (k) Extrelut 20 columns - Merck-11737 (EM-11737-1 VWR Scientific San Francisco CA 94120) Refill packages are also available without columns (Merck-11738)
- (l) Volumetric flasks - Glass 250 mL

- (m) Rotary flash evaporator - Buchi RE-120 or equivalent with water bath at 45-50 C
- (n) Culture tubes - 16 x 123 mm, screw-cap Teflon-lined (Scientific Products T-1358-1), used for the derivatization reaction
- (o) Tube heater - Kontes No K-720000, used for the derivatization reaction
- (p) N-Evap analytical concentrator - Organomation, or equivalent
- (q) Vortex - Super Mixer Model 1290 (Lab-Line)
- (r) C-18 cartridges - Sep-Pak (Waters Associates 51910)
- (s) Disposable Pasteur pipet - Glass, 9 x 0.7 mm od (VWR Scientific 14672-380)
- (t) Centrifuge tubes - Graduated 10-15 mL (Fisher Scientific 05-538-35B)
- (u) Syringes - Glass 10 mL equipped with Luer-Lok fitting (Fisher Scientific 14-823-15C)
- (v) Rheostat - Input 120 V output 0-120/140 V (Staco Energy Products Co Dayton OH 45403)
- (w) Syringe needles - Stainless steel 100 mm (Organomation 11305)
- (x) Wide-bore Luer connector - Special goosenecked syringe needle see Figure 4
- 63 (y) Gas chromatograph - Hewlett-Packard Model 5880A equipped with Ni electron capture detector

Reagents

- (a) Acetic anhydride - ACS certified 98% (Fisher Scientific)
- (b) Acetonitrile - Pesticide quality or equivalent (Mallinkrodt)
- (c) Acetylation mixture - Add 1 mL pyridine to 5 mL acetic anhydride Prepare fresh daily
- (d) Emulsifier - HOE S-1728 (ATA TH-1 Hoechst Aktiengesellschaft Analytical Laboratory 6230 Frankfurt (M) 80 Postfach 80 03 20)
- (e) Emulsifier solution - 1% HOE S-1728 in distilled water Dissolve 10.0 g HOE S-1728 in 1000 mL distilled water The emulsifier solution often needs purification as follows Partition 500 mL emulsifier solution with

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three 100 mL portions of hexane Place resultant aqueous solution on rotary evaporator with water bath at 45-50 C until all traces of hexane are removed

- (f) Ethyl acetate - Pesticide quality or equivalent (Mallinkrodt 3427)
- (g) Ethyl ether - Pesticide quality or equivalent (Mallinkrodt)
- (h) Ethyl ether-hexane (20+80)
- (i) Glacial acetic acid - ACS reagent grade or equivalent (Mallinkrodt 3121)
- (j) Glass wool - Treated with dimethyldichlorosilane (Cat No 4037 Alltech Associates/Applied Science Deertfield IL 60015) used for packing the silica gel minicolumn
- (k) Hexane - Pesticide quality or equivalent (Mallinkrodt 4159)
- (l) Hydrochloric acid - Concentrated ACS reagent grade
- (m) Methanol - Pesticide quality or equivalent (Mallinkrodt 5160)
- (n) Pyridine - ACS certified (Fisher Scientific P 368)
- (o) Reflux solution - Acetonitrile-concentrated HCl (90+10)
- (p) Silica gel - Merck 7734 Dry for ≥ 5 h at 130 C
- (q) Silica gel (3% water-deactivated) - Add 3 g distilled water to 97 g oven-dried (5 h) silica gel Let mixture equilibrate for ≥ 48 h on roller mill, or equivalent equipment
- (r) Sodium sulfate - Anhydrous granular (Eastman Kodak Co 842)
- (s) Toluene - Pesticide quality or equivalent (OmniSolv EM Merck TX 0737-1)
- (t) Fenoxaprop-ethyl analytical standard - Hoechst-Roussel Agri-Vet Co Somerville NJ 08876
- (u) Fenoxaprop analytical standard - Hoechst-Roussel Agri-Vet Co
- (v) HOE 054014 analytical standard - Hoechst-Roussel Agri-Vet Co
- (w) HOE 083312 analytical standard - Hoechst-Roussel Agri-Vet Co

Preparation of Standard Solutions

Stock solutions C and D are used for GC analysis, stock solutions G J and M are used for fortification

(Note - Wrap all stock solutions with aluminum foil and store in refrigerator)

HOE 083312 - Stock solution A - Weigh 100 0 mg HOE 083312 analytical standard into 800 mL volumetric flask Dilute to volume with toluene This solution contains 1 0 mg HOE 083312/mL Prepare fresh every 3 months, or as needed Stock solution B - Transfer 5 0 mL aliquot of stock solution A to 100 mL volumetric flask Dilute to volume with toluene This solution contains 50 0 µg HOE 083312/mL Prepare fresh every month, or as needed Stock solution C - Transfer 5 0 mL aliquot of stock solution B to 100 mL volumetric flask Dilute to volume with toluene This solution contains 2 5 µg HOE 083312/mL Prepare fresh every month or as needed Stock solution D - Transfer 4 0 mL aliquot of stock solution C to 100 mL volumetric flask Dilute to volume with toluene This solution contains 0 10 µg HOE 083312/mL Prepare fresh every month or as needed Make dilutions of stock solution D every week or as needed to calibrate gas chromatograph A typical set of dilutions is shown in Table 1

Fenoxaprop-ethyl - Stock solution E - Weigh 100 0 mg fenoxaprop-ethyl analytical standard into 100 mL volumetric flask Dilute to volume with toluene This solution contains 1 0 mg fenoxaprop-ethyl/mL Prepare fresh every 6 months or as needed Stock solution F - Transfer 5 0 mL aliquot of stock solution E to 100 mL volumetric flask Dilute to volume with toluene This solution contains 50 0 µg fenoxaprop-ethyl/mL Prepare fresh every month or as needed Stock solution G - Transfer 5 0 mL aliquot of stock solution F to 100 mL volumetric flask Dilute to volume with toluene This solution contains 2 5 µg fenoxaprop-ethyl/mL Prepare fresh every 2 months or as needed

Fenoxaprop - Stock solution H - Weigh 100 0 mg fenoxaprop analytical standard into 100 mL volumetric flask Dilute to volume with ethyl acetate This solution contains 1 0 mg fenoxaprop/mL Prepare fresh every 6 months or as needed Stock solution I - Transfer 5 0 mL aliquot of stock solution H to 100 mL volumetric flask Dilute to volume with ethyl acetate This solution contains 50 0 µg fenoxaprop/mL Prepare fresh every 2 months, or as needed Stock solution J - Transfer 5 0 mL aliquot of stock solution I to 100 mL volumetric flask Dilute to volume with ethyl acetate This solution contains 2 5 µg fenoxaprop/mL Prepare fresh every month or as needed

HOE 054014 - Stock solution K - Weigh 100 0 mg HOE 054014 into 100 mL volumetric flask Dilute to volume with ethyl acetate This solution contains 1 0 mg HOE 054014/mL Prepare fresh every 6 months or as needed Stock solution L - Transfer 5 0 mL aliquot of stock solution K to 100 mL volumetric flask Dilute to volume with ethyl acetate This solution contains 50 0 µg HOE 054014/mL Prepare fresh every 2 months or as needed Stock solution M - Transfer 5 0 mL aliquot of stock solution L to 100 mL volumetric flask Dilute to volume with ethyl acetate This solution contains 2 5 µg HOE 054014/mL Prepare fresh every month or as needed

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Table 1 Preparation of typical standard solutions for calibration of gas chromatograph

Concentration of standard solution prepared for injection		Stock solution diluted	Volume of aliquot taken for dilution, mg	Final dilution volume mL
ng/ μ L	pg/ μ L			
0 0020	2 0	D	2 0	100 0
0 0040	4 0	D	4 0	100 0
0 0060	6 0	D	6 0	100 0
0 0100	10 0	D	10 0	100 0
0 0250	25 0	C	1 0	100 0

Sample Preparation

Prepare homogeneous, finely ground analytical laboratory sample from field sample

Extraction

(Note - As a safety precaution it is essential that the reflux portion of the procedure be carried out in an efficiently operating fume hood)

(Note - Drier matrices especially rice straw soybean hay and some rice grain require analysis of a smaller analytical portion and addition of water to the reflux mixture See modification of the extraction procedure described in Analytical Notes (Petitioner))

Weigh 25 0 g portion of analytical sample (W) into 500 mL round-bottom flask equipped with $\frac{3}{4}$ 29/42 ground glass joint Add 80 mL reflux solution to flask Thoroughly homogenize solvent-matrix mixture in flask using high-speed Polytron mixer for $>1-2$ min Rinse Polytron blades with additional 20 mL reflux solution Add rinsings to round-bottom flask containing solvent-matrix mixture (Note - The total volume of reflux solution is 100 mL) Gently reflux solvent-matrix mixture for 6 h Reflux of solvent typically occurs in the first 2" of the reflux condenser Occasionally swirl extraction mixture during reflux

After reflux add 100 mL distilled water through top of reflux condenser Immediately filter warm solution through fluted filter paper without rinsing The volume of extract at this point is considered to be 225 mL (equivalent to 200 mL extraction solvent plus 25 g analytical sample V_1)

Extrelut Column Cleanup

Transfer 20 mL (T_1) aliquot of filtered extract to Extrelut column (Note - The Extrelut Column is used as received) Let filtered extract equilibrate with column matrix for 30 min After equilibration elute column with 50 mL hexane Discard hexane eluate (Note - Elution with >50 mL hexane has been found to elute portions of the compound of interest)

Elute hydrolysis product, HOE 054014, from column with 250 mL hexane-ethyl ether (8+2) Collect eluate in 500 mL round-bottom flask equipped with 24/40 ground glass joint (Note - It is helpful in this elution step to use an inverted 250 mL volumetric flask containing elution solvent Fill volumetric flask with solvent and invert onto top of Extrelut column This is especially helpful since the Extrelut column has no reservoir This technique ensures a continuous flow of elution solvent)

Concentrate Extrelut column eluate to ca 2 mL using rotary flash evaporator with water bath at 45-50 C Remove remaining hexane by adding small portions of ethyl acetate (ca 10 mL total) to round-bottom flask and evaporating to 2 mL after each addition (Note - It is important that no hexane remains)

Use ethyl acetate to quantitatively transfer contents of flask to 10 mL screw-cap culture tube (For soybean seeds rice grain, and rice straw use ethyl acetate to quantitatively transfer contents of flask to 10 mL graduated centrifuge tube, dilute to exactly 10 0 mL with ethyl acetate, and mix thoroughly transfer 5 0 mL aliquot to screw-cap culture tube)

Completely evaporate ethyl acetate with stream of nitrogen using N-Evap analytical concentrator and water bath at 45-50 C

Derivatization

Add exactly 1 0 mL acetylation mixture to residue in culture tube Tightly close tube with Teflon-lined screw cap and mix contents of tube thoroughly Place tube in tube heater at 130 C for 3 h (Note - It is important that the entire tube be within the heated area with the cap and Teflon liner outside the heated area) This reaction quantitatively converts HOE 054014 to HOE 083312

After derivatization remove capped tubes and let cool to room temperature

C-18 Sep-Pak Cartridge Cleanup

Cartridge preparation - Immediately before use elute C-18 Sep-Pak cartridge with 5 0 mL methanol (in short pulses), followed by 10 0 mL distilled water (Note - The cartridge should appear opaque with no air pockets The top of the cartridge should contain water (not air), and no attempt to remove residual water is needed)

Procedure - Draw 5 mL emulsifier solution into 10 mL glass syringe equipped with Luer fitting Attach 150 mm stainless steel Luer needle to syringe and then draw derivatization mixture into syringe Rinse walls of reaction vessel with 0 5 mL glacial acetic acid vortex contents of tube and draw contents into syringe containing emulsifier solution and derivatization mixture Finally draw 1 mL distilled water through needle into syringe Remove needle and vortex contents of syringe vigorously for ca 1 min with piston of syringe in downward position (Note - Care must be taken not to

lose solution through the Luer end of the syringe) This process destroys any residual acetic anhydride

Slowly press entire solution in syringe through shorter end of preconditioned C-18 Sep-Pak cartridge (Note - To avoid air passing onto cartridge, add 1-2 drops of solution in syringe to top of cartridge before elution) The derivative HOE 083312 remains on the cartridge Attach cartridge to vacuum and aspirate 10 mL distilled water through short end of cartridge Dry cartridge by vacuum for >5 min (Note - House vacuum is normally sufficient whereas water aspiration is typically insufficient An empty 10 mL syringe attached to the shorter end of the cartridge has been used successfully to aspirate the distilled water through the column The apparatus used in this technique is shown in Figure 4) Usually water removal from the Sep-Pak cartridge is not quantitative

After drying tap cartridge on flat surface to remove any residual water droplets (Note - The next steps are easiest to perform with a minimum amount of water present Thus it is essential to eliminate as much residual water as possible)

Draw 7 0 mL hexane into 10 mL glass syringe equipped with Luer fitting Attach short end of cartridge to syringe Hold syringe pointing straight down and press hexane gently through cartridge

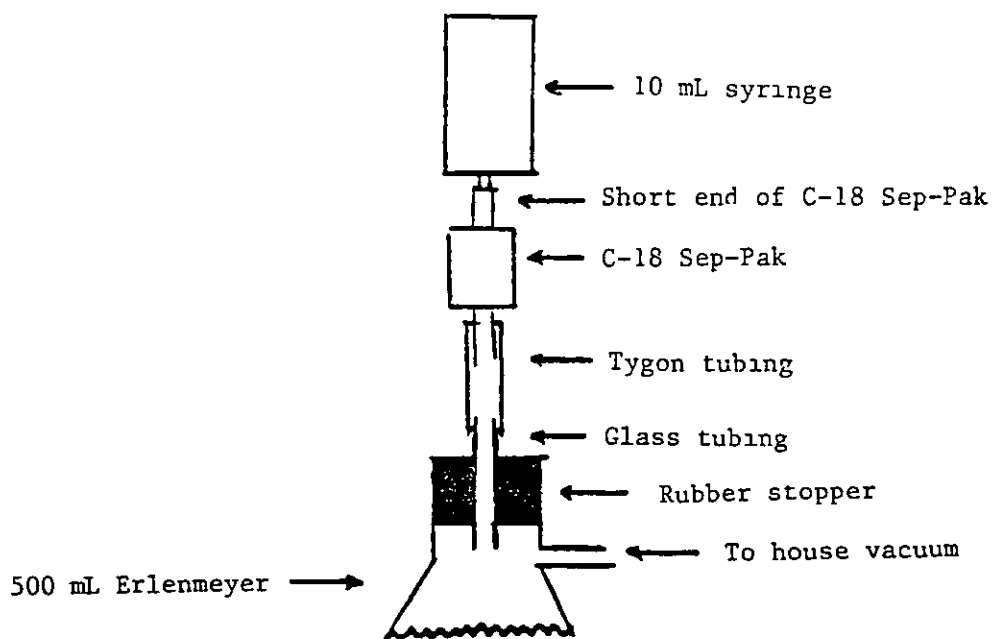


Figure 4 Washing of C-18 Sep-Pak cartridge

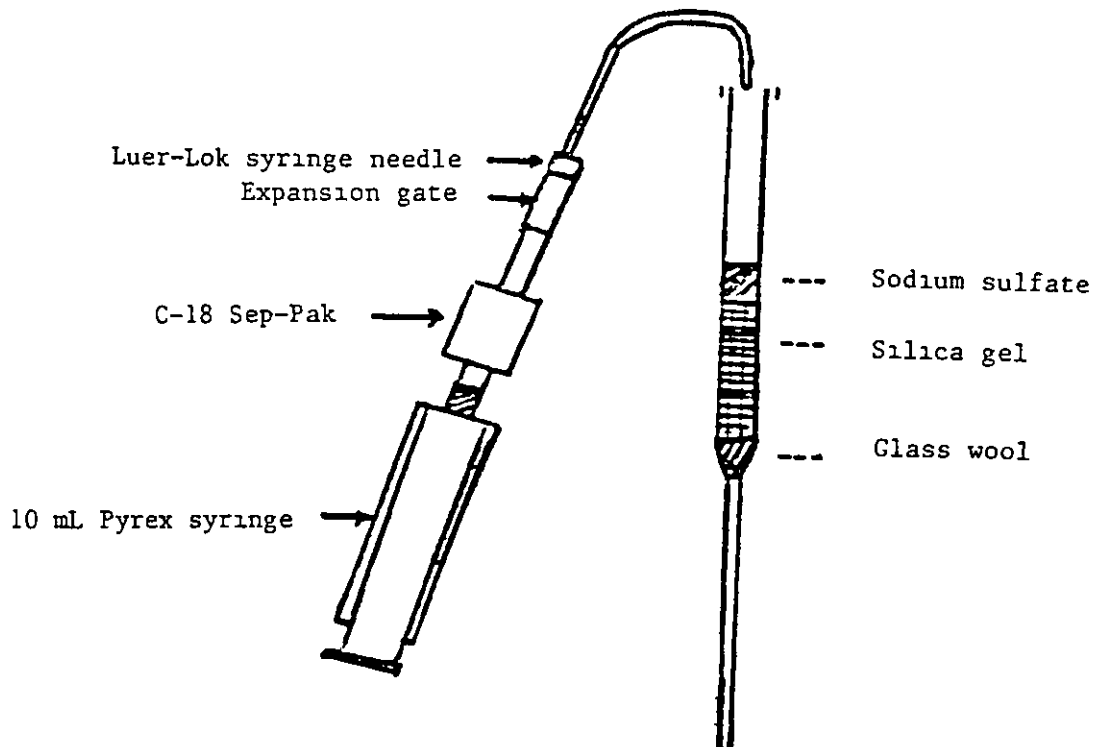


Figure 5 Assembly for transferring C-18 Sep-Pak cartridge eluate to silica gel minicolumn

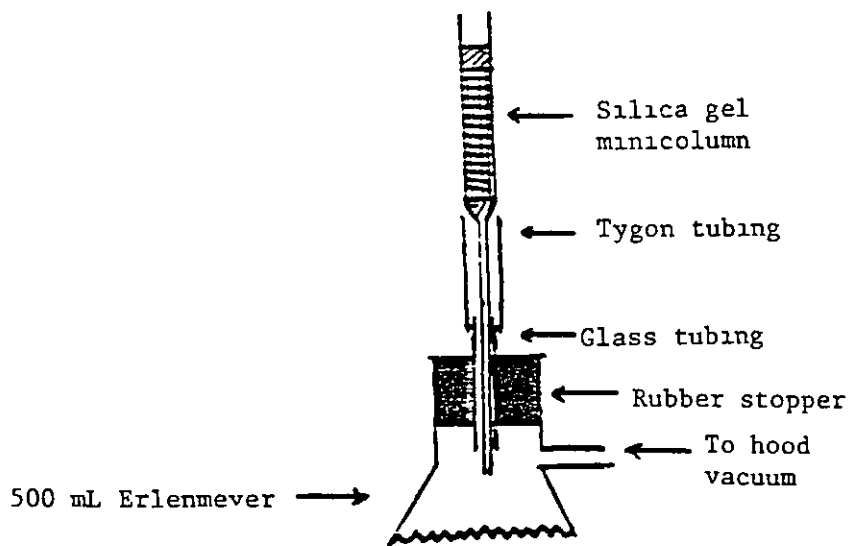


Figure 6 Removal of hexane from silica gel minicolumn

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As the hexane moves through the cartridge the remaining water is forced through. The first drops of eluate (amount depends on prior removal, typically 2 or 3 drops remain) are water and should be blotted onto filter paper. (Note - The water appears as a much darker liquid or as a meniscus at the exit end of the cartridge.)

Using assembly shown in Figure 5 transfer hexane eluate which contains HOE 083312 directly onto silica gel minicolumn.

Silica Gel Minicolumn Cleanup

Minicolumn preparation - Place silanized glass wool plug in bottom of 9" Pasteur pipet. Add 0.3 g 3% water-deactivated silica gel. Precondition column by washing with 5 mL hexane. Remove all air bubbles by gentle tapping. (Note - The column will appear opaque at this point.) While hexane is still above column surface add ca 0.2 g (5 mm) anhydrous sodium sulfate. Rinse column with another small portion (ca 3 mL) of hexane and let drain. (Note - It is not critical that the column continually contain hexane. However do not let the column stand for >1 h.)

Minicolumn characterization - Before performing any analyses characterize elution profile of silica gel column by adding HOE 083312 analytical standard (dissolved in hexane) and observing elution pattern. Effective cleanup and maximum recovery (95-100%) must be attained. The expected toluene elution volume is 2.5-3.0 mL.

Procedure - It is very important that additional water be excluded from the silica gel minicolumn. The sodium sulfate helps to do this. However a special elution technique has also been developed. Invert syringe and attach 100 mm goosenecked needle to long end of C-18 Sep-Pak cartridge. Invert syringe assembly (Figure 5) and press hexane slowly upward through cartridge transferring cartridge eluate directly onto silica gel minicolumn.

After last of hexane eluate has passed through sodium sulfate layer rinse column with three 2.0 mL portions of hexane. Discard all hexane fractions.

After hexane rinses have passed through column remove all hexane remaining on column by brief application of vacuum as shown in Figure 6.

Use toluene to elute HOE 083312 from column. Collect first 3.0 mL (or appropriate volume determined by column standardization) of eluate in 10 mL graduated centrifuge tube. Dilute eluate to suitable final volume (V_3) with toluene. Typically 5.0 mL is appropriate for fenoxaprop-ethyl fortifications at the 0.05 ppm level, 10.0 mL is appropriate for HOE 054014 fortifications at the 0.05 ppm level. (Note - These volumes also depend upon the sensitivity of the GC detector used.)

Gas Chromatography

Performance check - Compare response for HOE 083312 analytical standard in toluene with that for a fully processed control extract (V_3) fortified with the same amount of standard. The 2 responses must be within 5-10% of

one another for a calibration curve to be used for quantitation, otherwise the alternative method of calculation must be used with fortified control extracts in place of standard solutions

Operating conditions - 10' x 2 mm id packed column of 3% SP-2100 on 100/120 mesh Supelcoport, temperatures (C) - inlet 225 detector 320 column temperature program - 150 C for 10 min, ballistic program to 220 C with 15 min hold time, carrier argon-methane (95+5), carrier flow 30 mL/min, injection volume 5 0 µL, attenuation 2 x 11 chart speed 0 5 cm/min, minimum detection limit 5 pg HOE 083312 injected approximate retention time 3 5-5 0 min (Note - Column temperatures may be adjusted within a range of 10-15 C from the temperatures given to obtain optimal separation characteristics)

Calibration curve - Prepare initial calibration curve once instrument response is stable Prepare a calibration curve for every analytical series Inject 5 µL aliquots of standard solutions of appropriate concentrations (Table 1) into gas chromatograph, and measure peak heights (or areas) Construct calibration curve by plotting peak height (or area) vs nanograms of HOE 083312 for each standard solution injected

Determination - Inject 5 µL aliquot (T_4) of sample extract in toluene into gas chromatograph and measure peak height (or area) (Note - Bracket every 3-4 injections of sample extract with injections of standard solutions to maintain a continual check for shifts in sensitivity) Determine nanograms of HOE 083312 in injected aliquot by comparison with calibration curve

Calculate concentration of total residue in sample as fenoxaprop-ethyl equivalents

$$\text{ppm} = (\underline{A} \times \underline{F}) / \underline{B}$$

where \underline{A} = weight of HOE 083312 in injected aliquot (ng) \underline{F} = molecular weight (MW) correction factor 1 71 (MW of fenoxaprop-ethyl/MW of HOE 083312 = 361 8/211 6) and \underline{B} = weight of sample represented by injected aliquot of sample extract (mg)

$$\underline{B} = (\underline{W} \times \underline{T}_1 \times \underline{T}_4 \times \underline{AF}) / (\underline{V}_1 \times \underline{V}_3)$$

where \underline{W} = weight of sample taken for analysis (g) \underline{T}_1 = aliquot of filtered extract transferred to Extrelut column (mL) \underline{T}_4 = aliquot of sample extract injected (µL) \underline{AF} = fraction of concentrated eluate taken for derivatization (e g 0 5) \underline{V}_1 = final volume of reflux mixture (mL) (e g 225 mL for 25 g sample 100 mL reflux solution and 100 mL distilled water) and \underline{V}_3 = final volume of minicolumn eluate in toluene (mL)

Example of calculation for soybean seed

$\underline{B} = (25 \text{ g} \times 20 \text{ mL} \times 5 0 \text{ µL} \times 0 5) / (225 \text{ mL} \times 5 0 \text{ mL}) = 1 11 \text{ mg}$ soybean seed represented by injected aliquot of sample extract

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Alternative method of calculation - Inject 5 µL aliquot (\underline{T}_4) of sample extract in toluene into gas chromatograph and measure peak height (or area) Immediately inject 5 µL aliquot of standard solution of appropriate concentration into gas chromatograph, and measure peak height (or area) (Note - Peak heights (or areas) must be within 10-15% of one another and injection volumes must be identical) Calculate concentration of total residue in sample as fenoxaprop-ethyl equivalents

$$\text{ppm} = (\underline{P}_{\text{SPL}} \times \underline{W}_1 \times \underline{F} \times \underline{V}_1 \times \underline{V}_3) / (\underline{P}_{\text{STD}} \times \underline{W}_2 \times \underline{T}_1 \times \underline{T}_4 \times \underline{AF})$$

where $\underline{P}_{\text{SPL}}$ = peak height from injection of sample extract (mm), $\underline{P}_{\text{STD}}$ = peak height from injection of standard solution (mm) \underline{W}_1 = weight of HOE 083312 in injected aliquot (ng), and \underline{W}_2 = weight of sample taken for analysis (g), \underline{F} , \underline{V}_1 \underline{V}_3 \underline{T}_1 \underline{T}_4 and \underline{AF} are as defined previously

Fortified controls - To calculate total residue as fenoxaprop or HOE 054014 equivalents use the appropriate value of \underline{F} (MW correction factor)

$$\underline{F} \text{ (fenoxaprop)} = 1.58 \text{ (MW of fenoxaprop/MW of HOE 083312 = 333.7/211.3)}$$

$$\underline{F} \text{ (HOE 054014)} = 0.80 \text{ (MW of HOE 054014/MW of HOE 083312 = 169.6/211.3)}$$

Analytical Notes (Petitioner)

Modification of extraction procedure for drier matrices - Weigh 10.0 g portion of analytical sample (\underline{W}) into 500 mL round-bottom flask equipped with T 29/42 ground glass joint. Add 80 mL reflux solution plus 50 mL distilled water to flask. Continue with the procedure as described until end of reflux. After reflux, add 50 mL distilled water through top of reflux condenser. Immediately filter warm solution through fluted filter paper without rinsing. The volume of extract at this point is considered to be 210 mL (equivalent to 200 mL extraction solvent plus 10 g analytical sample, \underline{V}_1) Proceed with the method as described.

Method application - The method has been successfully applied to soybean matrices (seed forage and straw) soybean process fractions (seed meal hulls crude oil refined oil and soapstock) rice matrices (grain and straw) and rice process fractions

EPA COMMENTS

Recovery Studies (EPA)

Soybean samples fortified with fenoxaprop-ethyl fenoxaprop and HOE 054014 each at the 0 05 and 0 10 ppm levels were analyzed in triplicate by Method I The results of the method trial are summarized in Table 1

The GC operating conditions for the method trial were as follows Hewlett-Packard Model 5880A gas chromatograph equipped with ⁶³Ni electron capture detector and 10' x 2 mm id packed column of 3% SP-2100 on 100/120 mesh Supelcoport temperatures (C) - injector 225 detector 325 isothermal operation at 145 C, injection volume 4 5 µL, final volume of minicolumn eluate (V₃) 5 0 or 10 0 mL

Analytical Note (EPA)

When a new GC column is prepared it is important to condition it with Rejuv-8 (Supelco Inc Bellefonte PA 16823) actual sample extracts and nanogram quantities of HOE 083312 for several days before it is used

Table 1 Recovery of fenoxaprop-ethyl fenoxaprop and HOE 054014 from soybeans (EPA)

Compound added	Added ppm	Found ppm	Rec %
Fenoxaprop-ethyl	0	0 007 ^a	--
	0 05	0 039	78
	0 05	0 034	68
	0 05	0 039	78
	0 10	0 084	84
	0 10	0 080	80
	0 10	0 088	88
Fenoxaprop	0	--	--
	0 05	0 035	70
	0 05	0 039	78
	0 05	0 039	78
	0 10	0 072	72
	0 10	0 086	86
	0 10	0 074	74
HOE 054014	0	--	--
	0 05	0 042	84
	0 05	0 041	82
	0 05	0 040	80
	0 10	0 082	82
	0 10	0 088	88
	0 10	0 090	90

^aAppeared to be a random contamination rather than a recurring interference This value was not subtracted in the calculations