Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Endosulfan I

MRID #: 411641-01

Matrix: Soil

Analysis: GC/ECD

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STANDARD OPERATING PROCEDURE FOR DETERMINATION OF ENDOSULFANS IN SOIL

1. SCOPE

1.1. This standard operating procedure (SOP) describes the analysis of α-endosulfan, β-endosulfan, and endosulfan sulfate (hereafter referred to as "endosulfans") in soil.

2. SUMMARY

2.1. Up to 50 g of soil is serially extracted by tumbling with acetone. The acetone is combined with salted water and equilibrated with methylene chloride using an automated separatory funnel shaker. The extract may be cleaned up by gel permeation chromatography (GPC), Florisil, or silica gel adsorption chromatography. The final extract is concentrated after solvent substitution with hexane and analyzed by capillary column gas chromatography (GC) using an electron capture detector (ECD).

3. APPARATUS

3.1. Glassware. The required glassware must be solvent cleaned and heated at 400-500°C for at least 4 hours following SOP ASCC-50-019, or glassware may be cleaned as described in the SOP except for heating, then rinsed with methanol and methylene chloride.

3.1.1. Centrifuge bottles -- 200-mL with Teflon-lined screw cap

3.1.2. Kimax separatory funnel -- 2-L with a Teflon stopcock and stopper.

3.1.3. Graduated cylinders -- 1000-, 500-, and 50-mL

3.1.4. Kuderna-Danish equipment

3.1.4.1. Concentration tube -- 25-mL

3.1.4.2. Flask -- 500-mL

3.1.4.3. Macro-Snyder column -- 3-ball chambers

3.1.4.4. Micro-Snyder column -- 3-ball chambers

3.1.5. Collection flask -- 500-mL Erlenmeyer or round-bottom

3.1.6. Serological pipet -- 5-mL disposable

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3.1.7. Vials -- GPC with Teflon-lined septum

3.1.8. Vials -- 4-dram with Teflon-lined screw caps

3.1.9. Beakers -- 50 mL

3.2. Miscellaneous materials

3.2.1. Pyrex glass wool -- heated at 400-500°C for at least 4 hours.

3.2.2. Carborundum boiling chips -- heated at 400-500°C for at least 4 hours.

3.2.3. Water bath -- Blue M Magniwhirl or equivalent.

3.2.4. Analytical balance -- capable of weighing with an accuracy of ±0.0001 g.

3.2.5. Top-loading balance -- capable of weighing with an accuracy of ±0.01 g.

3.2.6. Nitrogen evaporation device -- N-Evap Organomation Associates, or equivalent, with constant temperature water bath. The nitrogen gas must be filtered through activated charcoal.

3.2.7. Peroxide test strips -- capable of detecting 1.5 mg/L peroxide.

3.2.8. Tumbler apparatus - capable of tumbling 200-mL centrifuge bottles end-over-end at a constant rate.

3.2.9. Separatory funnel shaker -- capable of holding eight 2-L separatory funnels and shaking them with a rocking motion to achieve thorough mixing of separatory funnel contents (available from Eberbach Co., Ann Arbor, Michigan).

3.2.10. Centrifuge - IEC Model 2K or equivalent.

3.2.11. GPC System - Set up system as described in SOP ASCC-50-102. Define fraction collection zone as shown in Figure 1. These times correspond to the interval between

the end of the bis(2-ethylhexyl)phthalate peak and the end of the pentachlorophenol peak in the GPC standard. These times may change slightly; therefore, the GPC standard must be run before any samples to ensure the proper collection times. Normally the fraction eluting between 31 and 44 min contains the endosulfans and is collected.

3.2.12. Gas Chromatograph -- analytical system complete with GC suitable for use with capillary columns and all required accessories including syringes, analytical columns, gases, and electron capture detector.

3.2.12.1. Capillary column -- 30 meters long x 0.25 mm I.D. SPB-5 bonded fused silica column, 0.25 μm film thickness (available from Supelco). Alternative columns may be used in accordance with the provisions described in Section 5.2.

3.2.12.2. Detector -- ECD. Alternative detectors, including a mass spectrometer, may be used in accordance with the provisions described in Section 5.2.

3.3. Reagents

3.3.1. Solvents -- Burdick and Jackson distilled-in-glass grade methylene chloride, unpreserved ethyl ether, hexane, and ethyl acetate.

3.3.2. Reagent water -- Millipore water or distilled water from Magnetic Springs Water Company (Columbus, Ohio) or equivalent.

3.3.3. Sodium sulfate -- granular, anhydrous, heated at 400-500°C for at least 4 hours.

3.3.4. Florisil -- 60 to 100 mesh, J. T. Baker or equivalent, activated by heating at 140°C overnight.

3.3.5. Silica gel -- 100-200 mesh, chromatographic grade, Sigma Chemical Company or equivalent, activated by heating at 140°C overnight.

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3.3.6. 2,3,4,5,2'-Pentachlorobiphenyl -- >95% purity, for use as internal standard (Note: another polychlorinated biphenyl isomer, 2,3,4,2',5'-pentachlorobiphenyl, can also be successfully substituted as the internal standard).

3.3.7. Stock standard solution of endosulfans (1 mg/mL) -- The stock standard solution is prepared from pure standard materials as in the following example:

3.3.7.1. Prepare stock standard solution by accurately weighing 10 mg each of α-endosulfan, β-endosulfan, and endosulfan sulfate, dissolving the materials in ethyl acetate and diluting to volume with ethyl acetate in a 10-ml volumetric flask. Larger quantities may be prepared if necessary. If compound purity is certified at 95% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

3.3.7.2. Transfer the stock standard solution into a screw-cap vial with a Teflon-lined cap. Store at 4±2°C and protect from light.

3.3.7.3. The stock standard solution must be replaced after three months or sooner if GC-ECD analyses indicate a problem.

3.3.8. Spike solution (50 μg/mL) -- Make a 5:100 dilution of the stock standard solution (i.e. 5 mL of the stock standard solution (Section 3.3.7.) into a 100-mL volumetric flask, and dilute to volume with ethyl acetate). Addition of 100 μL of the spike solution to 50 g of soil results in a concentration of 100 μg/kg for each individual endosulfan. Transfer the soil spike solution into a screw-cap vial with a Teflon-lined cap. Store at 4±2°C and protect from light. The spike solution must be replaced after three months or sooner if comparison GC-ECD analyses indicate a problem.

3.3.9. Internal standard spike solution (0.05 mg/mL) -- Prepare the internal standard spiking solution by accurately weighing 5 mg of pure 2,3,4,5,2'-pentachlorobiphenyl, dissolving the compound in hexane, and diluting to volume

with hexane in a 100-mL volumetric flask. The amounts of 2,3,4,5,2'-pentachlorobiphenyl and hexane may be scaled up or down as long as the final concentration remains at 0.05 mg/mL. Transfer the internal standard spiking solution to a Teflon-lined screw-top bottle and store at room temperature. Addition of 5 µL of the internal standard spiking solution to 1 mL of sample extract yields an internal standard concentration of 0.25 µg/mL.

4. CALIBRATION

4.1. Establish retention times of each analyte and the internal standard. Calibrate the GC-ECD using the internal standard method.

4.2. Internal standard calibration procedure --

4.2.1. Prepare calibration solutions containing 2.5, 5, 10, 25, 50, 100, and 250 ng/mL each of α-endosulfan, β-endosulfan, and endosulfan sulfate and 0.25 µg/mL of internal standard. Prepare calibration solutions by adding volumes of the spike solution (Section 3.3.8.) to a volumetric flask. Add the appropriate constant amount of the internal standard solution (Section 3.3.9.) to each calibration standard, and dilute to volume with hexane.

4.2.2. Inject 1-2 µL of each calibration standard and tabulate the relative response for each analyte (RR_a) to an internal standard using the equation:

$$RR_a = A_a/A_{is}$$

where: A_a = analyte peak area, and
A_{is} = internal standard peak area.

Generate a calibration curve of analyte concentration response, RR_a, versus analyte concentration in the extract in ng/mL.

4.2.3. The working calibration curve must be verified on each working shift by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that analyte.

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5. QUALITY CONTROL

5.1. The minimum quality control requirements for this program consist of the following: an initial demonstration of laboratory capability; the analysis of spiked control samples (prepared in the field) as a continuing check on sample integrity; the analysis of background control samples (prepared in the field) as a continuing check on sample cross-contamination; the analysis of spiked process blanks (prepared in the analytical laboratory) as a continuing check on analytical method performance; and the analysis of process blanks (prepared in the analytical laboratory) as a continuing check on laboratory contamination.

5.2. In recognition of the rapid advances occurring in chromatography, the analyst is permitted to modify GC columns, GC conditions, or detectors to improve the separations or lower the cost of measurements. In addition, the analyst is also permitted to introduce a cleanup procedure in addition to GPC, Florisil adsorption chromatography, or silica gel adsorption chromatography to permit lower detection limits in a specific soil sample.

5.2.1. Each time such modifications are made, the laboratory must demonstrate acceptable method performance by extracting four representative soil samples, three spiked at 5-15 times the estimated method detection limit and one unspiked. The average recovery of each endosulfan must be between 70 and 130 percent, and the relative standard deviation of the three measurements must be equal to or less than 20 percent. Alternatively, the demonstration described in Section 5.2.2. can be substituted.

5.2.2. If a lower method detection limit is claimed, the laboratory must demonstrate acceptable method performance by extracting four representative soil samples, three spiked at the estimated method detection limit and one unspiked. The average recovery of each endosulfan should be between 70 and 130 percent, and the relative standard deviation of the three measurements should be equal to or less than 20 percent. The level of interferences detected as one of the endosulfans in the unspiked soil must be less than half of the claimed method detection limit.

5.3. Assessing Laboratory Performance -- The laboratory must, on an ongoing basis, analyze at least one spiked process blank per sample set. A sample set consists of 22 samples, one process blank, and one spiked process blank.

5.3.1. Combine all solvents listed in Sections 6.2. and 6.3. in a tumbler bottle, spike with 100 µL of the spike solution (Section 3.3.8.) and process and analyze to determine the concentration of each analyte in the final extract (A). Calculate percent recovery for each analyte (Ri) as (100 x A)%/T, where T is the known true concentration of the spike.

5.3.2. Monitor the percent recovery (R_i) for each analyte. The recoveries should be within ±30% of the true value. If the recovery of analyte falls outside the designated reasonable range, the laboratory performance for that analyte is judged to be out of control, and the source of the problem must be immediately identified and resolved before continuing analyses. The analytical results for that analyte in samples is suspect and must be so labelled. All results for that analyte in that sample set must also be labelled suspect.

5.4. Assessing Sample Integrity -- Spiked control samples, prepared in the field will be analyzed on a regular basis.

5.4.1. Monitor and report all data from the spiked samples.

5.4.2. If the recovery of any analyte falls outside the range specified in Section 5.3.2. and the laboratory performance for that analyte is judged to be in control, the recovery problem encountered with the dosed sample is judged to be matrix-related, not system-related. The result for that analyte in unspiked samples is labelled suspect/matrix to indicate that the results were suspect due to matrix effects.

5.5. Assessing Laboratory Contamination -- Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. This is accomplished by the analysis of a method blank and unspiked control samples.

5.5.1. A method blank is prepared by placing 100 mL of acetone into a 200-mL centrifuge bottle and proceeding with the steps described in Sections 6.3. through 6.12. A method blank is prepared and analyzed for each sample set (Section 5.3.) or when there is a change in reagents as a continuing check on laboratory contamination. The level of interferences detected as one of the endosulfans in the method blank must be less than half of the claimed method detection limit.

5.5.2. Unspiked control samples, prepared in the field, will be analyzed on a regular basis. Monitor and report all data from the unspiked samples. Detectable levels of any of the endosulfans may indicate sample cross-contamination during handling, shipping or storage.

6. PROCEDURE

6.1. Weigh up to 50 g of the sample into a 200-mL centrifuge bottle. Record the sample weight to the nearest 0.1 g in the laboratory record book. If the sample is a field spike sample, transfer the entire sample into the 200-mL centrifuge bottle and record the sample weight to the nearest 0.1 g.

6.2. Immediately after the sample has been removed from the sample container, place 5 to 10 g of sample in a tared beaker for the determination of the dry weight and record the wet weight to the nearest 0.1 g. (Do not determine the dry weight of a field spike.) Place the beaker in a 105-110°C drying oven for 40-56 hours. Remove the beaker and let it cool in a desiccator. Weigh the dried sample and record the dry weight to the nearest 0.1 g.

6.3. Add 100 mL of acetone to the centrifuge bottle; tumble the bottle end-over-end for 30 min. Remove the bottle from the tumbler and centrifuge for 10 min. Decant the organic layer into a 2-L separatory funnel containing 1 L of reagent water and 100 g NaCl. Add 100 mL of clean acetone to the centrifuge bottle and repeat the procedure.

6.4. Add 300 mL of methylene chloride to the separatory funnel. Shake and vent the separatory funnel until there is no release of vapor upon venting. Place the separatory funnel in an automatic

separatory funnel shaker and shake for 30 min. Complete mixing of the organic and aqueous phases should be observed within 2 min after starting the shaker.

6.5. Remove the separatory funnel from the shaker and place in a ringstand. Allow the organic layer to separate from the aqueous layer for a minimum of 10 min. If separation does not occur, 50-100 mL methylene chloride may be added to the sample to facilitate phase separation. Collect the methylene chloride extract in a 500-mL flask containing approximately 5 g anhydrous sodium sulfate. Swirl the flask to dry the extract; if the sodium sulfate is not free flowing, more sodium sulfate must be added to absorb excess water. Allow the sample to remain in contact with the drying agent for 15 min.

6.6. Assemble a K-D concentrator by attaching a 25-mL concentrator tube to a 500-mL flask. Decant the methylene chloride extract into the K-D concentrator. Rinse the sodium sulfate with two approximately 25-mL portions of methylene chloride; decant the rinses into the K-D concentrator.

6.7. Add 1-2 clean boiling chips to the evaporative flask and attach a macro-Snyder column which has been pre-wetted with methylene chloride. Place the K-D apparatus in a 65-70°C water bath; the concentrator tube should be partially immersed in the hot water and the flask should be bathed with hot vapor. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume reaches 5 mL, remove the K-D apparatus from the bath and allow it to cool for at least 10 minutes.

6.8. Remove the macro-Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methylene chloride. Dilute the sample to 25 mL with methylene chloride. Transfer the sample to a vial and refrigerate.

6.9. GPC cleanup -- This cleanup may not be necessary depending on the sample.

6.9.1. Transfer ~10 mL of extract from 6.8. into a GPC vial.

6.9.2. Inject 5 mL of the sample extract onto the GPC system following SOP ASCC-50-102. The amount of sample that is injected onto the GPC column represents 10 g of wet soil. Collect the fraction containing the endosulfans (Section 3.2.11.) in a K-D tube equipped with a 250 mL flask

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6.9.3. Add 1-2 clean boiling chips to the evaporative flask and place a prewetted macro-Snyder column on the K-D apparatus. Concentrate the sample to approximately 2 mL in a 65-70°C water bath; the concentrator tube should be partially immersed in the hot water and the flask should be bathed with hot vapor. Remove the K-D apparatus from the water bath and allow it to cool.

6.9.4. Add 5 mL of hexane and a clean boiling chip to the sample. Concentrate the sample to approximately 2 mL in a 85-90°C water bath. Add 5 mL hexane and reconcentrate to the apparent volume of 0.5 mL. Allow the sample to cool and adjust the volume to 1 mL with hexane. A nitrogen evaporator may be used to concentrate the sample.

6.10. Florisil cleanup -- This cleanup may not be necessary depending on the sample.

6.10.1. Dilute extract from 6.9.4. to 5 mL with hexane. If GPC clean-up was not performed, place 5 mL of extract from 6.8. and 5 mL of hexane into a K-D tube. Concentrate the sample to 2 mL using a micro-snyder column. Add 10 mL hexane and reconcentrate to 2 mL. Dilute to 5 mL with hexane.

6.10.2. Add 1 g of Florisil which has been thoroughly wetted with hexane to a serological pipet containing a plug of glass wool in the tip. Do not allow the Florisil to become exposed to the air during the fractionation procedure. When the liquid level is just above the adsorbent, apply the sample and begin collecting eluate in K-D tube. Rinse the concentrator tube with 2 mL of 1:1 hexane ethyl ether and add the rinse to the column; repeat.

6.10.3. Apply 6 mL of 50% ethyl ether in hexane to the column.

6.10.4. Concentrate the eluate to approximately 0.5 mL in a water bath or under a stream of nitrogen. Dilute to 2 mL with hexane.

6.11. Silica gel cleanup -- This cleanup may not be necessary depending on the sample.

6.11.1. Prepare the sample as described in 6.10.1.

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6.11.2. Add 1 g of 1.5% deactivated silica gel which has been thoroughly wetted with hexane to a serological pipet containing a plug of glass wool in the tip. Do not allow the silica gel to become exposed to the air during the fractionation procedure. When the liquid level is just above the adsorbent, apply the sample; begin collecting eluate in K-D tube. Rinse the concentrator tube with 2 mL of 1:1 hexane ethyl ether and add the rinse to the column; repeat.

6.11.3. Apply 6 mL of 50% ethyl ether in hexane to the column.

6.11.4. Concentrate the eluate to approximately 0.5 mL in a water bath (K-D) or under a stream of nitrogen; dilute the extract to 2 mL with hexane.

6.12. Spike the sample with 10 µL of the internal standard solution (Section 3.3.9.) and mix on a vortex mixer. Store extract at 4±2°C until analysis by GC-ECD. After analysis by GC-ECD, reseal the sample in the GC vial with a new septa and store at -10±2°C or lower.

7. GAS CHROMATOGRAPHY

7.1. Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in Table 1 are retention times observed using this method. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of Section 5.2. are met.

7.2. Calibrate the system daily as described in Section 4. The standards and extracts must be in hexane.

7.3. Inject 1-2 µL of the sample extract. Record the resulting peak size in height units.

7.4. If the response for the peak exceeds the calibrated working range of the system, dilute the extract, adjust the internal standard concentration by adding additional internal standard spike solution (Section 3.3.9.), and reanalyze.

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8. CALCULATIONS

8.1. Calculate the dry weight (DW) of the sample using the following equation:

$$DW = WW_S \times DW_a/WW_a$$

where WW_S = the wet weight of the processed sample as measured in Section 6.1., DW_a = the dry weight of the aliquot described in Section 6.2., and WW_a = the wet weight of the aliquot described in Section 6.2.

8.2. Calculate analyte concentrations in the sample extract (C_e), in ng/mL from the relative response of the analyte to the internal standard (RR_a) using the calibration curve described in Section 4. Calculate analyte concentrations in the original sample (C), in µg/kg using the equation:

$$C = \frac{C_e}{(DW / 5)}$$

8.3. For samples processed as part of a set where the laboratory control standard recovery falls outside of the control limits in Section 5, data for the affected analytes must be labelled as suspect.

9. RESULTS

9.1. In soil samples collected in Georgia, a detection limit of 10 µg/kg was demonstrated for α-endosulfan, β-endosulfan, and endosulfan sulfate. Recoveries of α-endosulfan, β-endosulfan, and endosulfan sulfate spiked into the soil at the 10 µg/kg level were 132±23 percent, 104±17 percent, and 92±12 percent, respectively. Peaks interfering with endosulfans were present at less than half the detection limit.

9.2. An example of a chromatogram generated from the 50 ng/mL calibration solution is given in Figure 2; this calibration level represents approximately 5 µg/kg in a soil sample. Examples of chromatograms generated from analyses of the Georgia soil, unspiked and spiked with endosulfans at the 10 µg/kg level, are shown in Figures 3 and 4, respectively.

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TABLE 1. SUGGESTED CHROMATOGRAPHIC CONDITIONS

Analyte	Chemical Abstracts Registry No.	Retention Time, min (a)
α-Endosulfan	959-98-8	40.8
β-Endosulfan	33213-65-9	43.6
Endosulfan sulfate	1031-07-8	45.7
2,3,4,2',5'-Pentachlorobiphenyl (internal standard)	--	42.0

(a) Suggested GC conditions:

Column:	30 m long x 0.25 mm I.D. DB-5 bonded fused silica column, 0.25 μm film thickness (J&W)
Alt. Column:	30 m DB-608
Injection volume:	2 μL splitless with 45 second delay
Carrier gas:	He @30 cm/sec linear velocity
Injector temp:	250°C
Detector temp:	320°C
Oven temp:	Hold 60°C for 1 minute, program from 60°C-220°C at 20°C/minute, program from 220°C at 4°C/minute
Alt. Oven temp:	Program from 60°C to 300°C at 4°C/minute
Detector:	ECD

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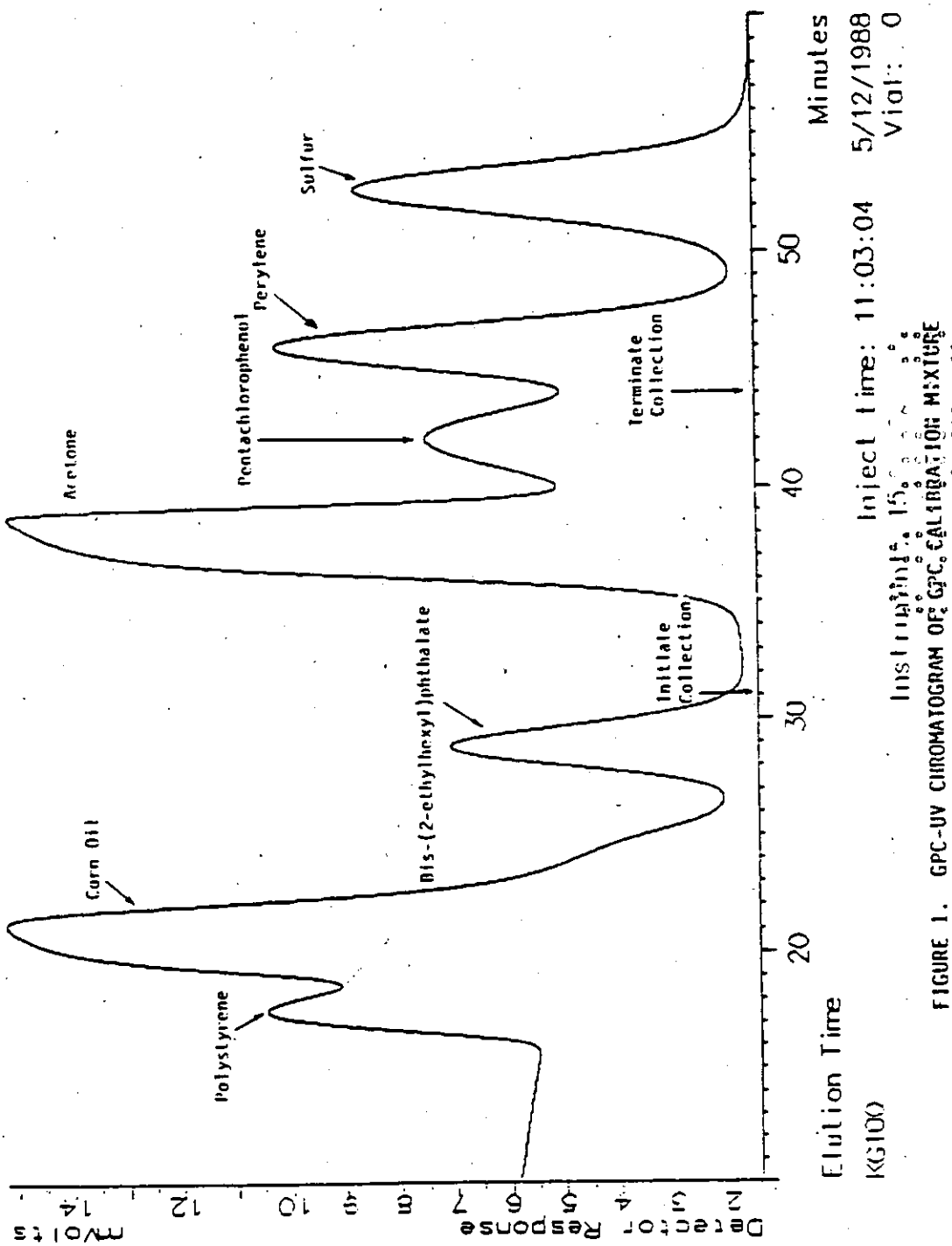

FIGURE 1. GPC-UV CHROMATOGRAM OF GPC CALIBRATION MIXTURE

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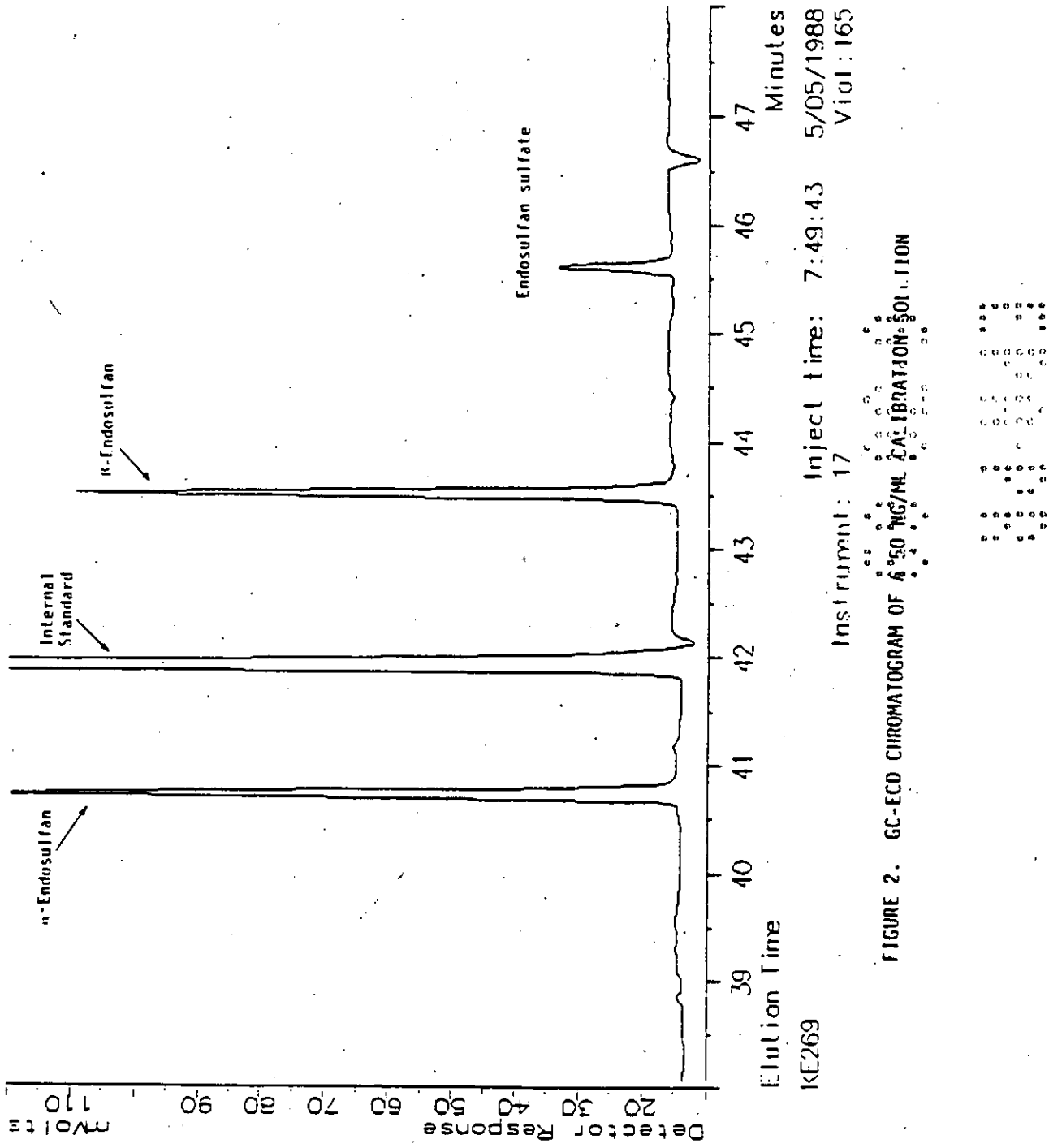

FIGURE 2. GC-ECD CHROMATOGRAM OF A 50 NG/ML CALIBRATION SOLUTION

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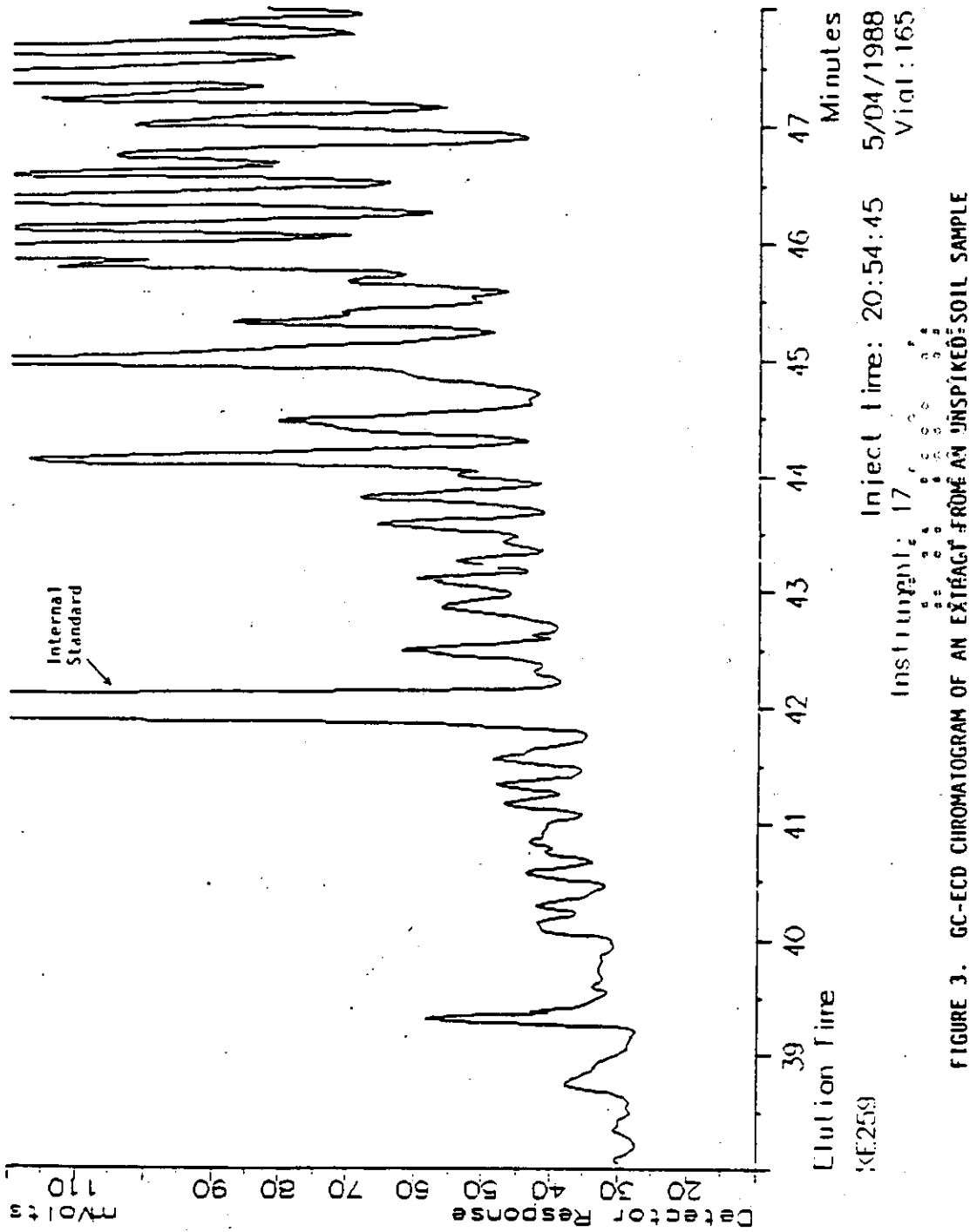

FIGURE 3. GC-ECD CHROMATOGRAM OF AN EXTRACT FROM AN UNSPIKED SOIL SAMPLE

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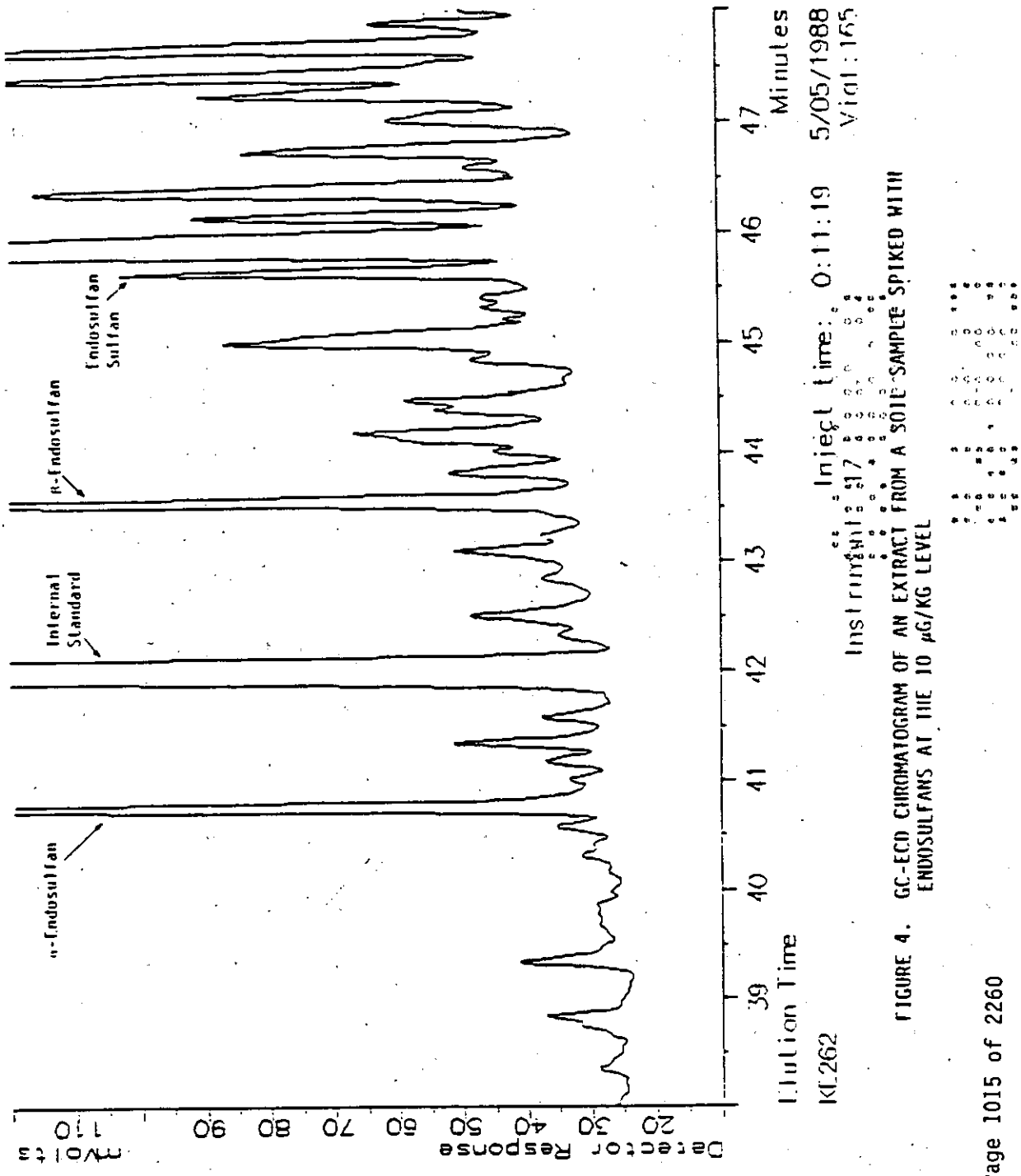

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FIGURE 4. GC-ECD CHROMATOGRAM OF AN EXTRACT FROM A SOIL SAMPLE SPIKED WITH ENDOSULFANS AT THE 10 µG/KG LEVEL

Soil

Chromatograms KN388 through KN394 are calibration chromatograms for alpha- and beta-endosulfan and endosulfan sulfate. The endosulfans are calibrated at 2.5, 5.0, 10, 25, 50, 100, and 250 ng/mL. The peak heights for each endosulfan was divided by the peak height of the internal standard. Calibration plots were generated by the computer and follow the standard chromatograms. The equation of the best line through the data is also given.

Chromatograms KN489 through KN493 are soil samples. The computer uses peak height ratios from these samples and calculates the final sample concentration in ng/mL from the calibration plot. This value is adjusted using the Standard and Sample Weights and Factors 3 and 4 shown on each report. The concentration is multiplied by Standard Weight and Factor 3 and divided by Sample Weight and Factor 4. The values used for these factors are as follows:

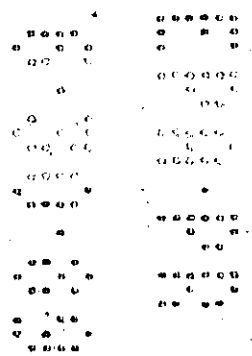
Standard Weight =	final sample volume in mL before further dilution.
Sample Weight =	100. This is a requirement of the software for Internal Standard calculations.
Factor 3 =	Sample dilution factor times sample split factor.
Factor 4 =	dry sample weight in grams.

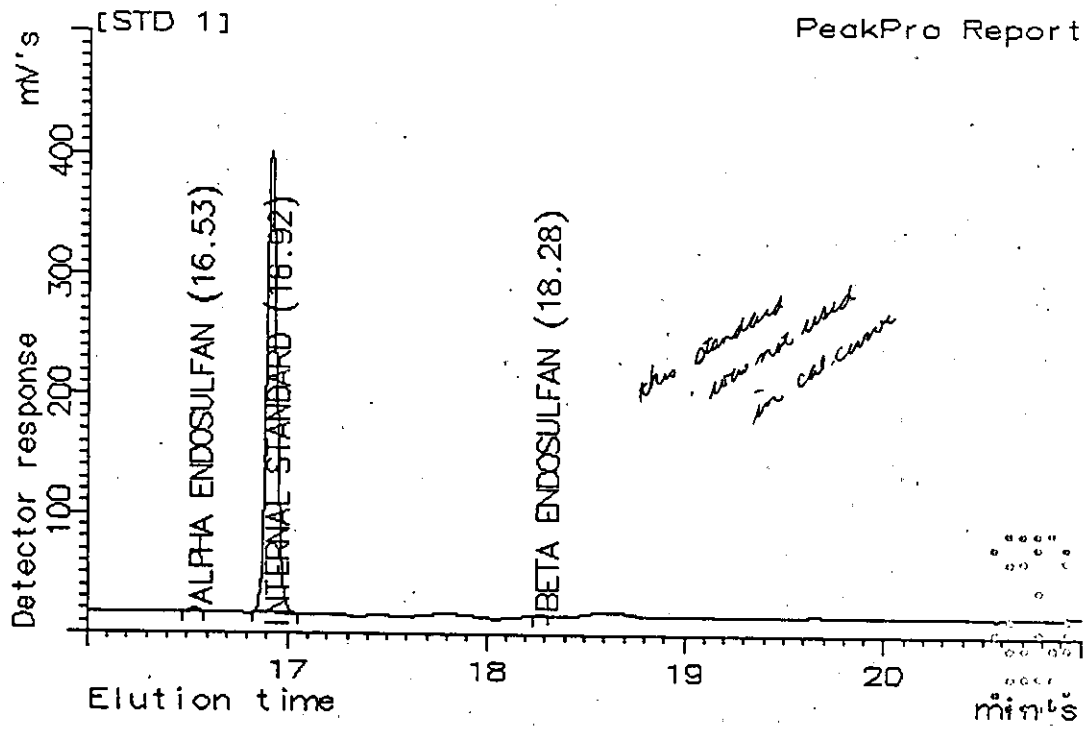
Units for the final calculated result are:

$$\frac{ng}{mL} * \frac{ml}{g} = \frac{ng}{g} = \frac{ug}{kg}$$

Sample KN493 is a field spike and is treated slightly differently. Factor 4 is 1000 (resulting in an assumed sample mass of 1 kg) in order to calculate total micrograms of spiked added.

A calibration check sample is analyzed with every 5 to 10 samples to make sure that the instrument performance does not change with time. Sample KN494 is such a check at 25 ng/mL. The Factors do not include any dilution, card area, or sample volume data to yield results in ng/mL.





INTERNAL STANDARD HEIGHT CALIBRATION

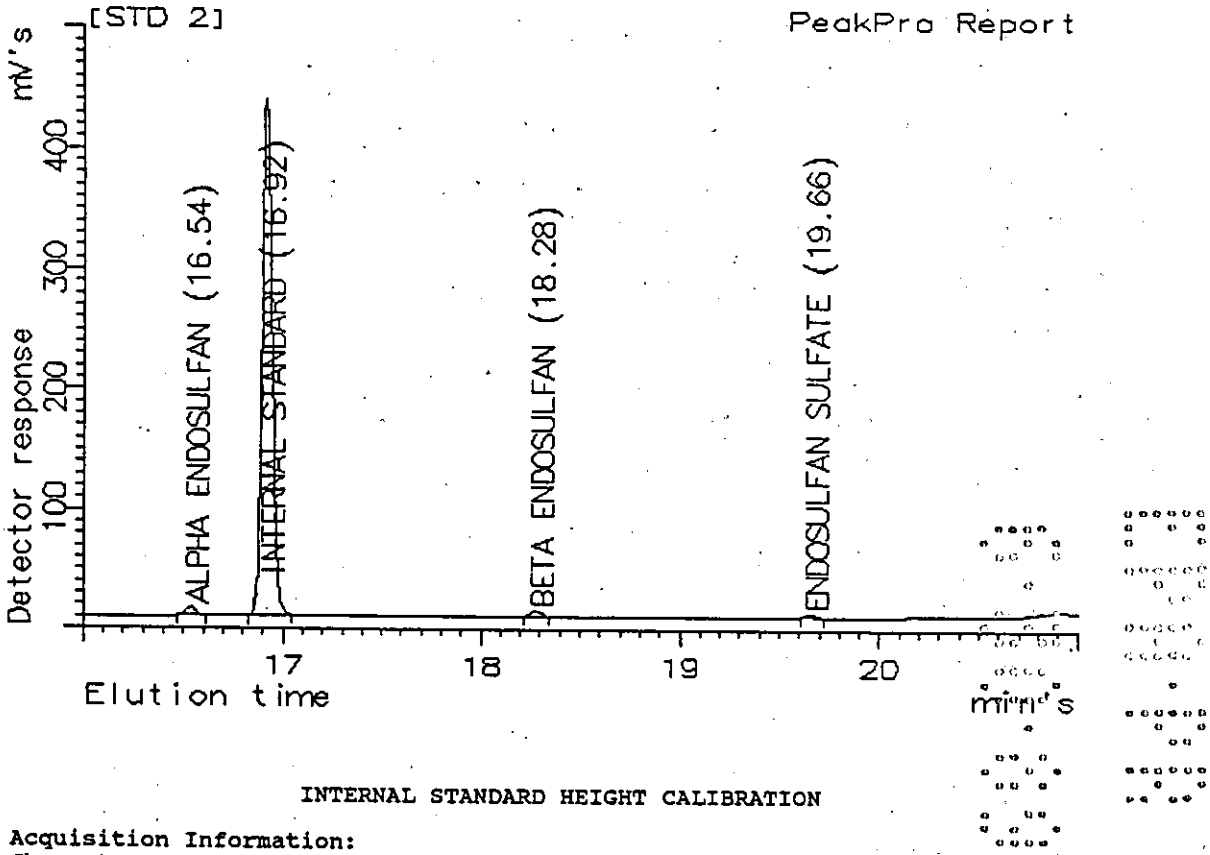
Acquisition Information:
Chromatogram: KN388 43481-60-04 2.5 NG/ML STD 8:04:06 2/23/1989
AC Method: 1510 Inst 19 Vial # 0

Analysis Information:
AN Method: GC1520 [STD 1] 7:32:43 2/24/1989
Analysis Method revision number: 55
Analyst: KIM ANDREWS Channel 0
RRF update code: Replace
RRT update code: Check

Testing Conditions
COLUMN: SPB-5 30 METER
OVEN: 60(1) - 220/20; 220 - 280/4

Component Name	RRT	RRF	Pk	NG/ML	Area	Height
ALPHA ENDOSULFAN	16.53	n/a	BCB	2.500	8.787	2.873
INTERNAL STANDARD	16.92I	1.000	BCB	1.000	1311.287	377.019
BETA ENDOSULFAN	18.28	n/a	BCB	2.500	3.001	1.116
ENDOSULFAN SULFATE	19.66					
Total				6.000	1323.076	381.008

KS



INTERNAL STANDARD HEIGHT CALIBRATION

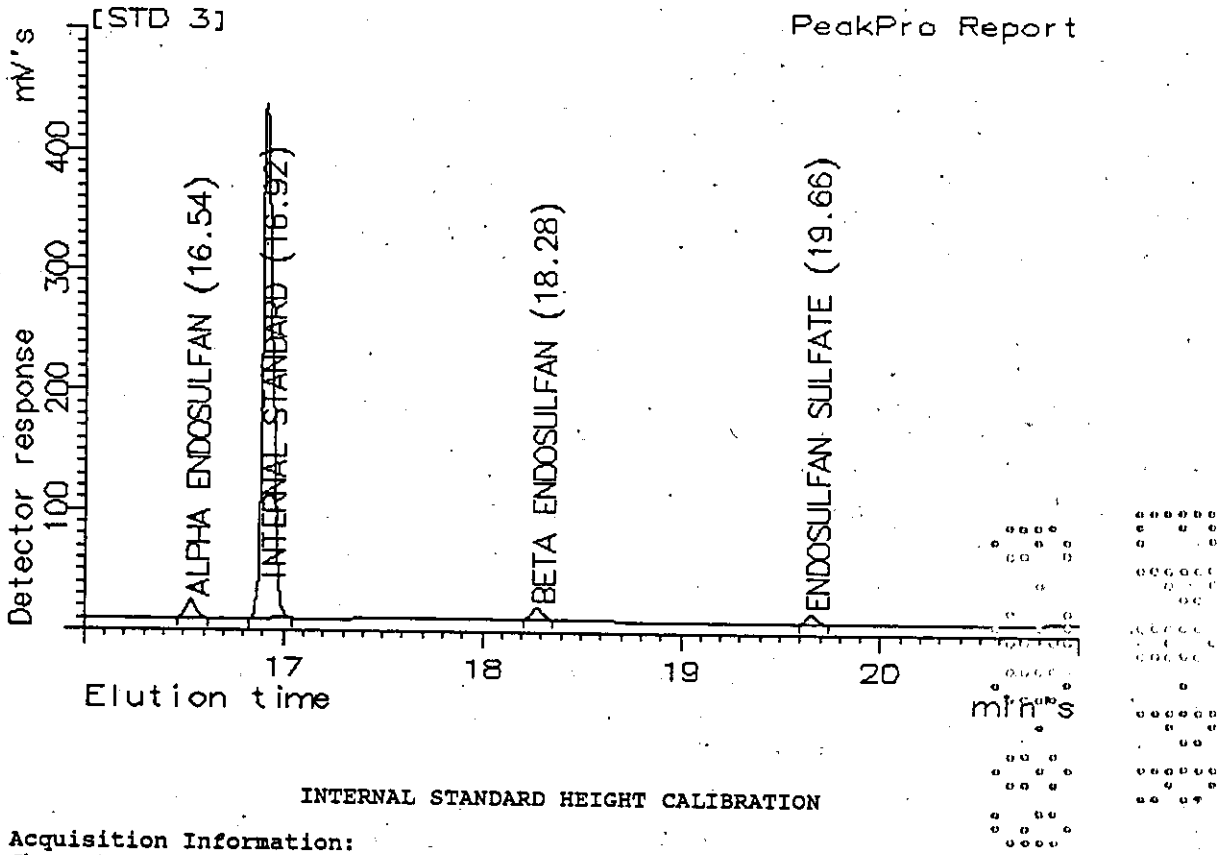
Acquisition Information:
Chromatogram: KN389 43481-60-05 5 NG/ML STD 8:33:20 2/23/1989
AC Method: 1510 Inst 19 Vial # 0

Analysis Information:
AN Method: GC1520 [STD 2] 7:33:37 2/24/1989
Analysis Method revision number: 55
Analyst: KIM ANDREWS Channel 0
RRF update code: Replace
RRT update code: Check

Testing Conditions
COLUMN: SPB-5 30 METER
OVEN: 60(1) - 220/20; 220 - 280/4

Component Name	RRT	RRF	Pk	NG/ML	Area	Height
ALPHA ENDOSULFAN	16.54	n/a	BCB	5.000	23.760	6.900
INTERNAL STANDARD	16.92I	1.000	BCB	1.000	1463.850	423.854
BETA ENDOSULFAN	18.28	n/a	BCB	5.000	15.857	4.544
ENDOSULFAN SULFATE	19.66	n/a	BCB	5.000	8.790	2.696
Total				16.000	1512.257	437.995

104



INTERNAL STANDARD HEIGHT CALIBRATION

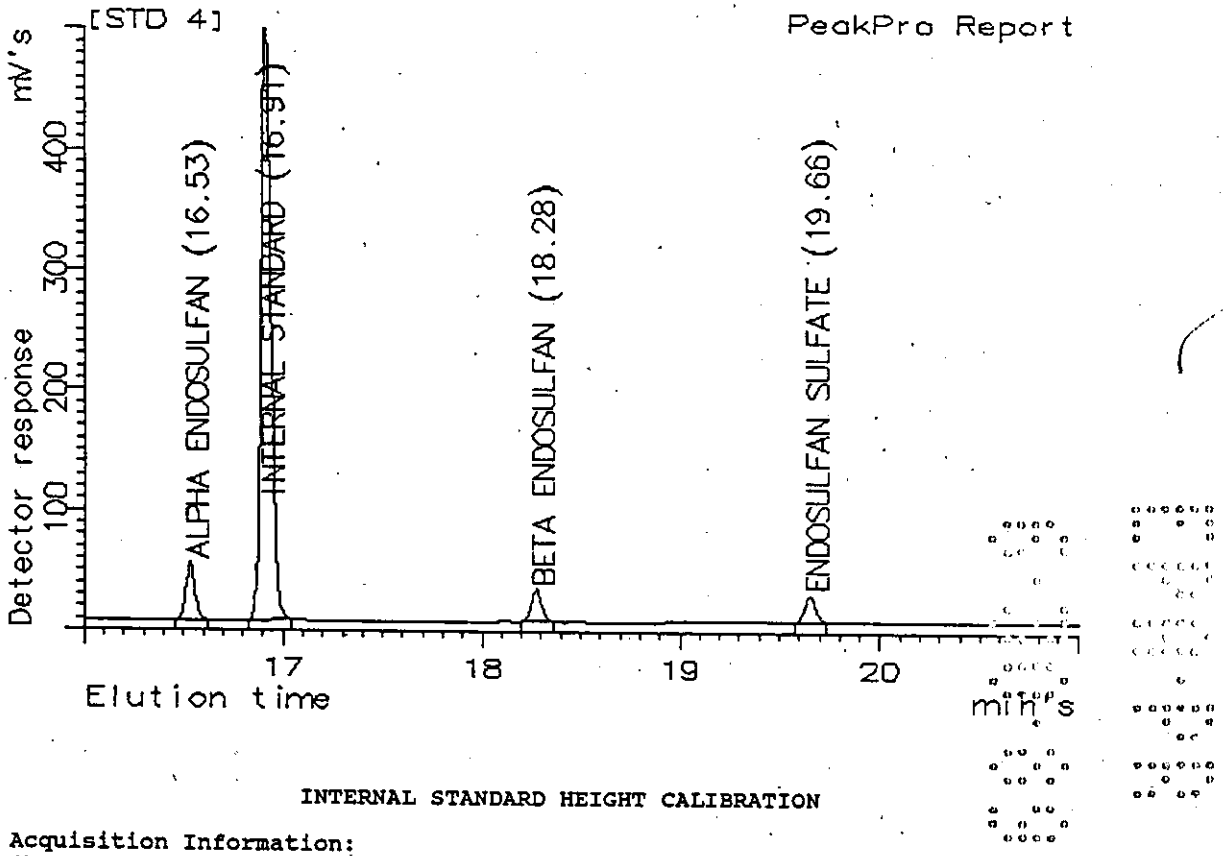
Acquisition Information:
Chromatogram: KN390 43481-60-06 10 NG/ML STD 9:02:36 2/23/1989
AC Method: 1510 Inst 19 Vial # 0

Analysis Information:
AN Method: GC1520 [STD 3] 7:34:42 2/24/1989
Analysis Method revision number: 55
Analyst: KIM ANDREWS Channel 0
RRF update code: Replace
RRT update code: Check

Testing Conditions
COLUMN: SPB-5 30 METER
OVEN: 60(1) - 220/20; 220 - 280/4

Component Name	RRT	RRF	Pk	NG/ML	Area	Height
ALPHA ENDOSULFAN	16.54	n/a	BCB	10.000	50.982	14.675
INTERNAL STANDARD	16.92I	1.000	BCB	1.000	1449.325	421.548
BETA ENDOSULFAN	18.28	n/a	BCB	10.000	34.153	9.276
ENDOSULFAN SULFATE	19.66	n/a	BCB	10.000	26.030	6.932
Total				31.000	1560.490	452.431

KA



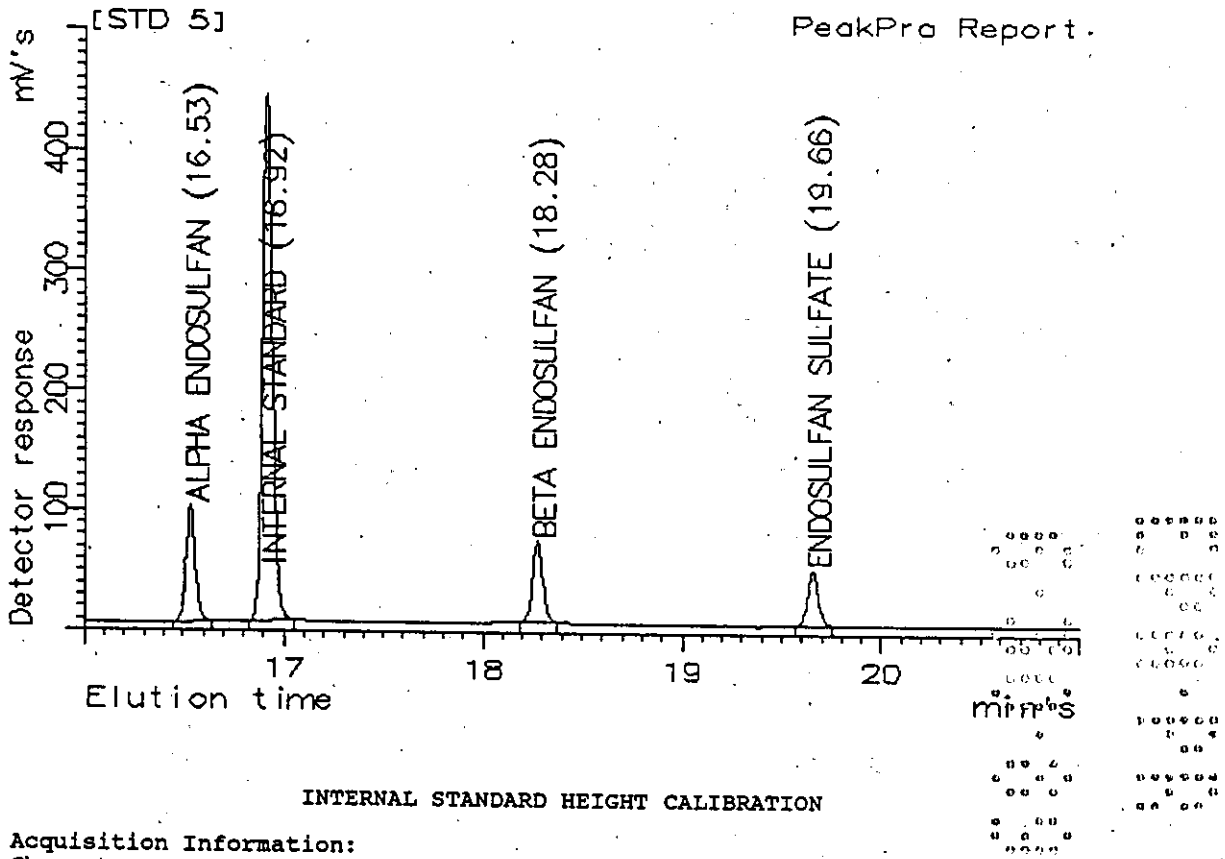
INTERNAL STANDARD HEIGHT CALIBRATION

Acquisition Information:
Chromatogram: KN391 43481-60-07 25 NG/ML STD 9:31:56 2/23/1989
AC Method: 1510 Inst 19 Vial # 0

Analysis Information:
AN Method: GC1520 [STD 4] 7:35:54 2/24/1989
Analysis Method revision number: 55
Analyst: KIM ANDREWS Channel 0
RRF update code: Replace
RRT update code: Check

Testing Conditions
COLUMN: SPB-5 30 METER
OVEN: 60(1) - 220/20; 220 - 280/4

Component Name	RRT	RRF	Pk	NG/ML	Area	Height
ALPHA ENDOSULFAN	16.53	n/a	BCB	25.000	157.982	48.072
INTERNAL STANDARD	16.91I	1.000	BCB	1.000	1723.507	498.464
BETA ENDOSULFAN	18.28	n/a	BCB	25.000	96.573	26.412
ENDOSULFAN SULFATE	19.66	n/a	BCB	25.000	80.522	21.529
Total				76.000	2058.585	594.477



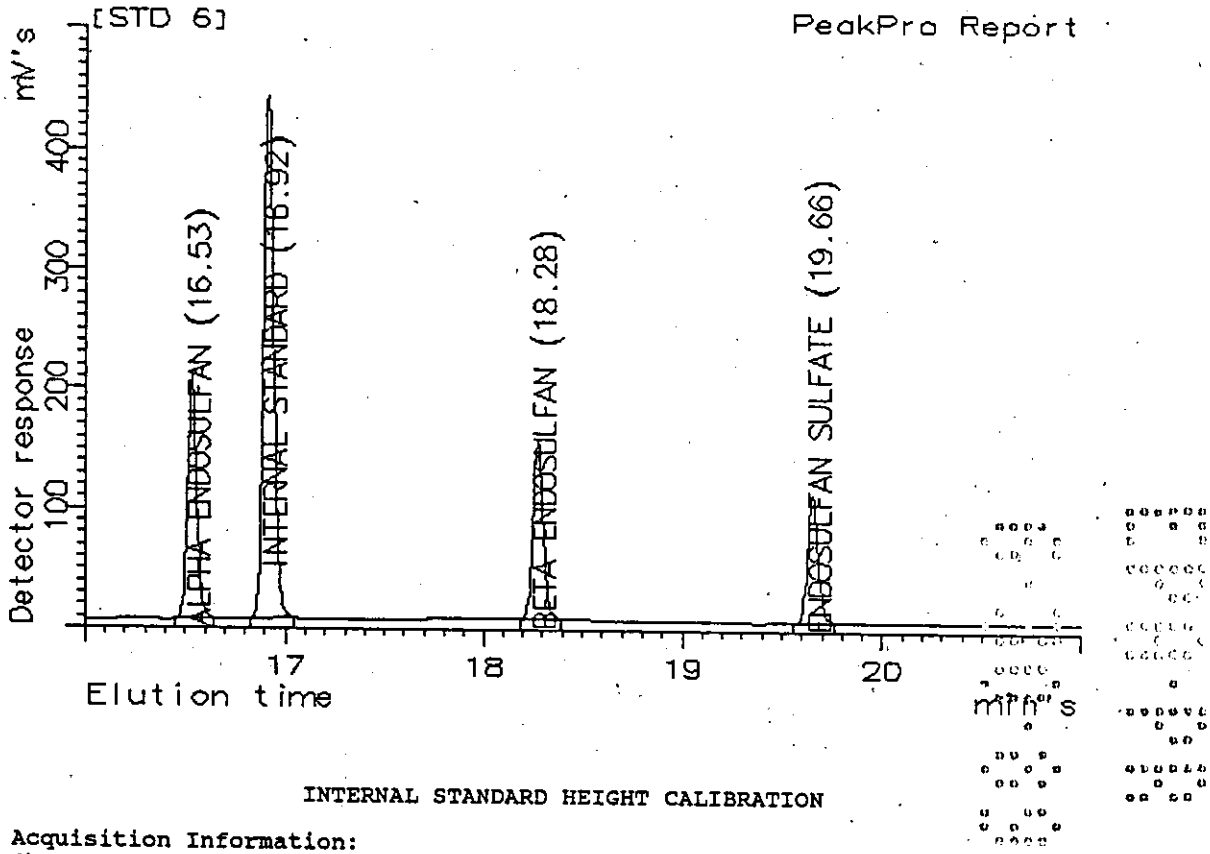
INTERNAL STANDARD HEIGHT CALIBRATION

Acquisition Information:
Chromatogram: KN392 43481-60-08 50 NG/ML STD 10:01:16 2/23/1989
AC Method: 1510 Inst 19 Vial # 0

Analysis Information:
AN Method: GC1520 [STD 5] 7:37:07 2/24/1989
Analysis Method revision number: 55
Analyst: KIM ANDREWS Channel 0
RRF update code: Replace
RRT update code: Check

Testing Conditions
COLUMN: SPB-5 30 METER
OVEN: 60(1) - 220/20; 220 - 280/4

Component Name	RRT	RRF	Pk	NG/ML	Area	Height
ALPHA ENDOSULFAN	16.53	n/a	BCB	50.000	312.264	96.184
INTERNAL STANDARD	16.92I	1.000	BCB	1.000	1490.975	434.955
BETA ENDOSULFAN	18.28	n/a	BCB	50.000	239.878	66.998
ENDOSULFAN SULFATE	19.66	n/a	BCB	50.000	166.451	45.028
Total				151.000	2209.569	643.166



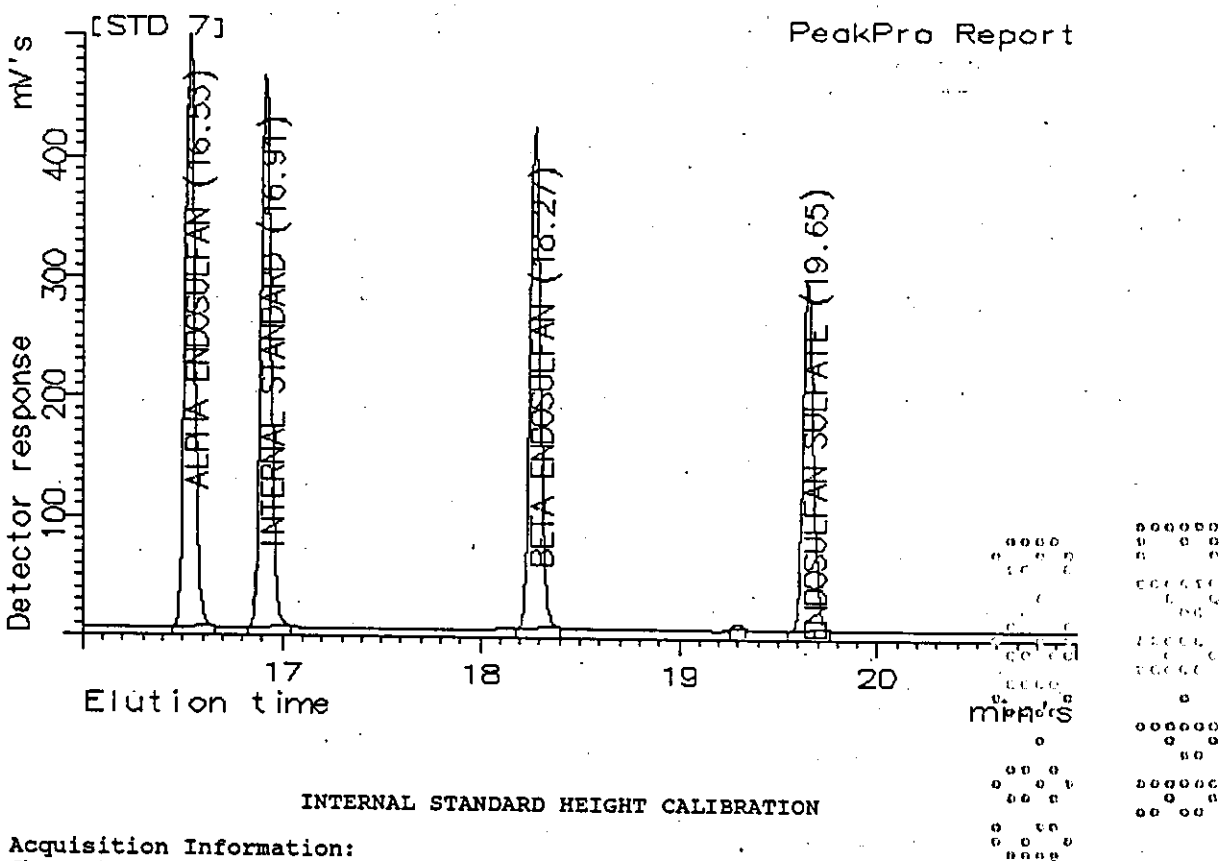
INTERNAL STANDARD HEIGHT CALIBRATION

Acquisition Information:
Chromatogram: KN393 43481-60-09 100 NG/ML STD 10:30:37 2/23/1989
AC Method: 1510 Inst 19 Vial # 0

Analysis Information:
AN Method: GC1520 [STD 6] 7:38:05 2/24/1989
Analysis Method revision number: 55
Analyst: KIM ANDREWS Channel 0
RRF update code: Replace
RRT update code: Check

Testing Conditions
COLUMN: SPB-5 30 METER
OVEN: 60(1) - 220/20; 220 - 280/4

Component Name	RRT	RRF	Pk	NG/ML	Area	Height
ALPHA ENDOSULFAN	16.53	n/a	BCB	100.000	646.388	200.370
INTERNAL STANDARD	16.92I	1.000	BCB	1.000	1482.735	430.592
BETA ENDOSULFAN	18.28	n/a	BCB	100.000	528.796	148.290
ENDOSULFAN SULFATE	19.66	n/a	BCB	100.000	384.149	104.817
Total				301.000	3042.067	884.069



INTERNAL STANDARD HEIGHT CALIBRATION

Acquisition Information:
Chromatogram: KN394 43481-60-10 250 NG/ML STD 10:59:54 2/23/1989
AC Method: 1510 Inst 19 Vial # 0

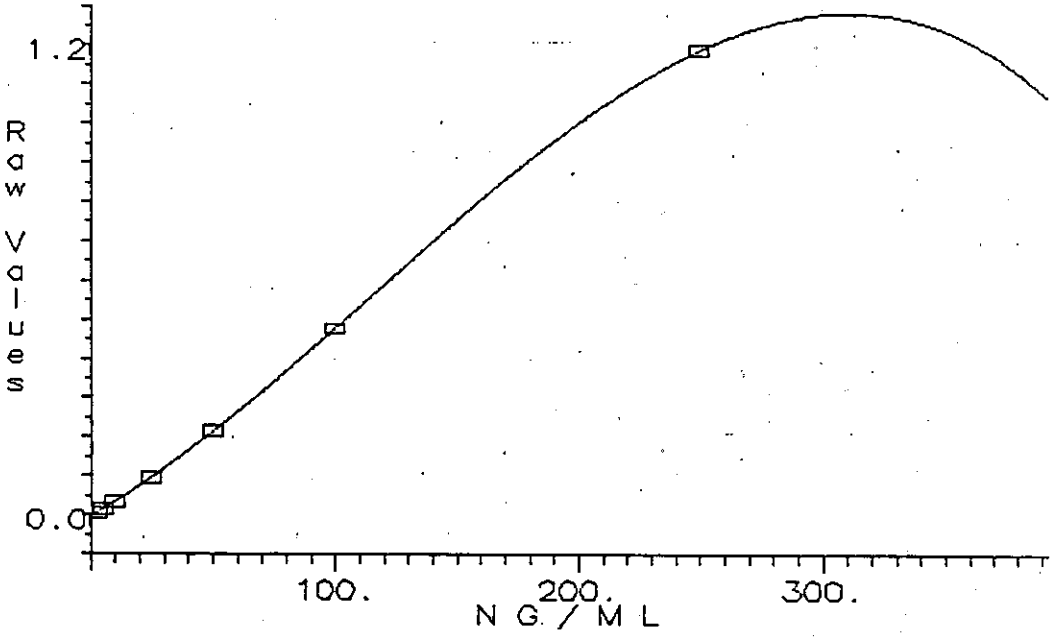
Analysis Information:
AN Method: GC1520 [STD 7] 7:39:04 2/24/1989
Analysis Method revision number: 55
Analyst: KIM ANDREWS Channel 0
RRF update code: Replace
RRT update code: Check

Testing Conditions
COLUMN: SPB-5 30 METER
OVEN: 60(1) - 220/20; 220 - 280/4

Component Name	RRT	RRF	Pk	NG/ML	Area	Height
ALPHA ENDOSULFAN	16.53	n/a	BCB	250.000	1711.211	520.092
INTERNAL STANDARD	16.91I	1.000	BCB	1.000	1581.591	455.344
BETA ENDOSULFAN	18.27	n/a	BCB	250.000	1497.710	414.750
ENDOSULFAN SULFATE	19.65	n/a	BCB	250.000	1061.805	287.744

KA

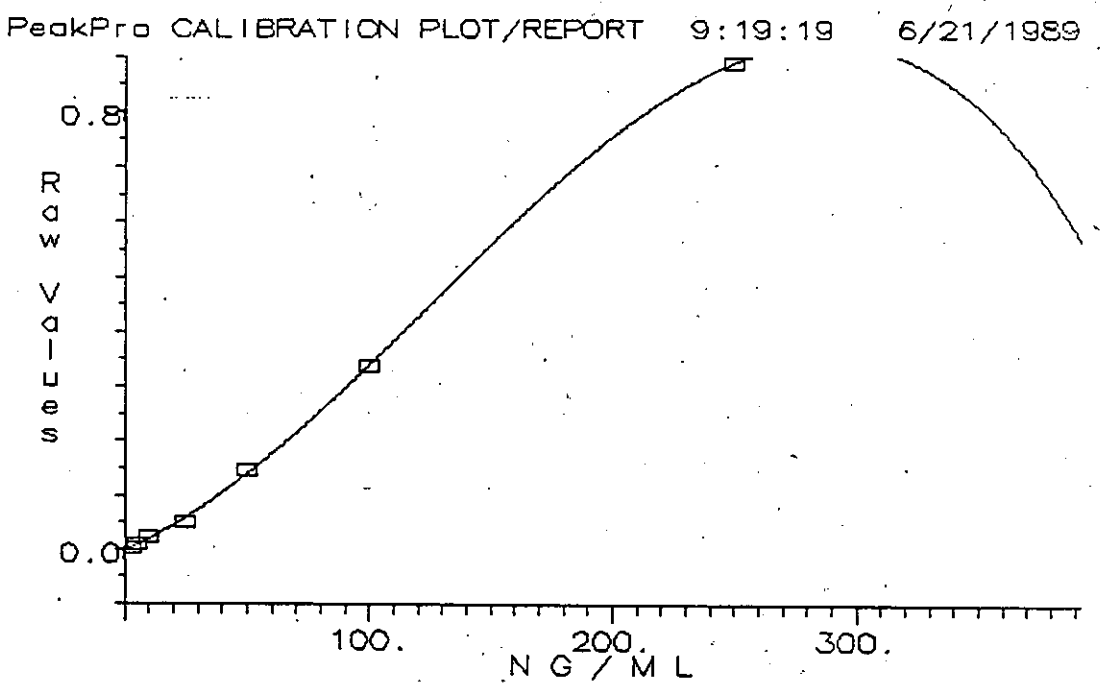
PeakPro CALIBRATION PLOT/REPORT 9:18:39 6/21/1989



Analysis method: 1190
Method Title: ENDOSULFAN COMPOUNDS - INSTRUMENT 19
Component Name: ALPHA ENDOSULFAN

Third degree polynomial fit
Polynomial Y = -0.0028 + 0.0036x + 0.0000x^2 - 0.0000x^3
RMS Deviation: 0.0019

Calibration Level		NG/ML	Raw Values
1	STD 1	2.500	0.0076
2	STD 2	5.000	0.0163
3	STD 3	10.000	0.0348
4	STD 4	25.000	0.0945
5	STD 5	50.000	0.2175
6	STD 6	100.000	0.4775
7	STD 7	250.000	1.1874

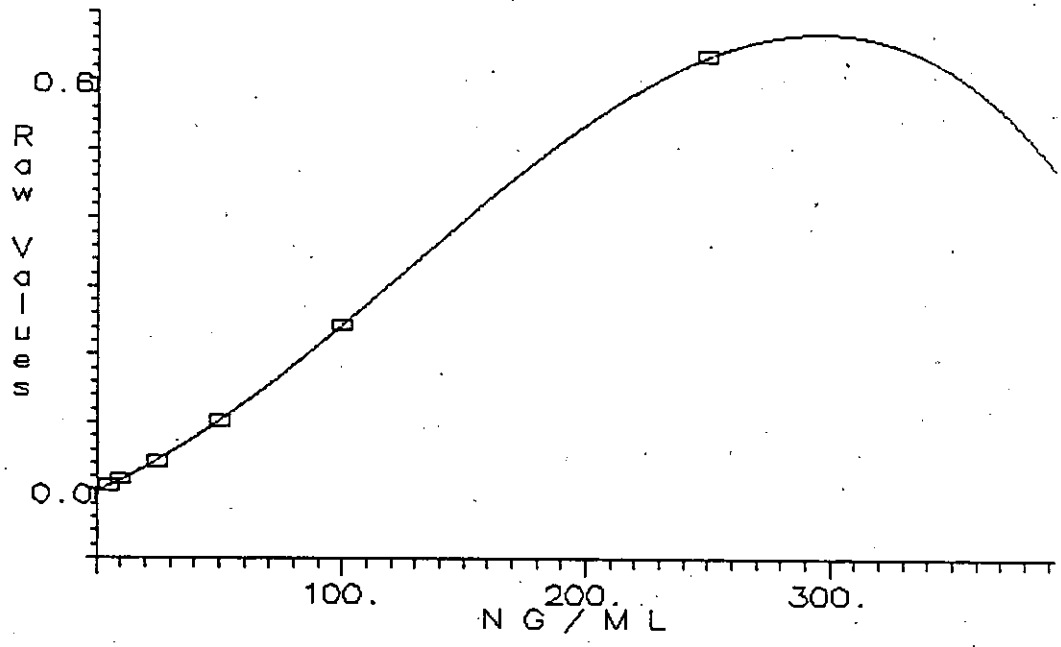


Analysis method: 1190
Method Title: ENDOSULFAN COMPOUNDS - INSTRUMENT 19
Component Name: BETA ENDOSULFAN

Third degree polynomial fit
Polynomial Y = -0.0018 + 0.0020x + 0.0000x^2 - 0.0000x^3
RMS Deviation: 0.0044

	Calibration Level	NG/ML	Raw Values
1	STD 1	2.500	0.0030
2	STD 2	5.000	0.0107
3	STD 3	10.000	0.0220
4	STD 4	25.000	0.0507
5	STD 5	50.000	0.1458
6	STD 6	100.000	0.3391
7	STD 7	250.000	0.8892

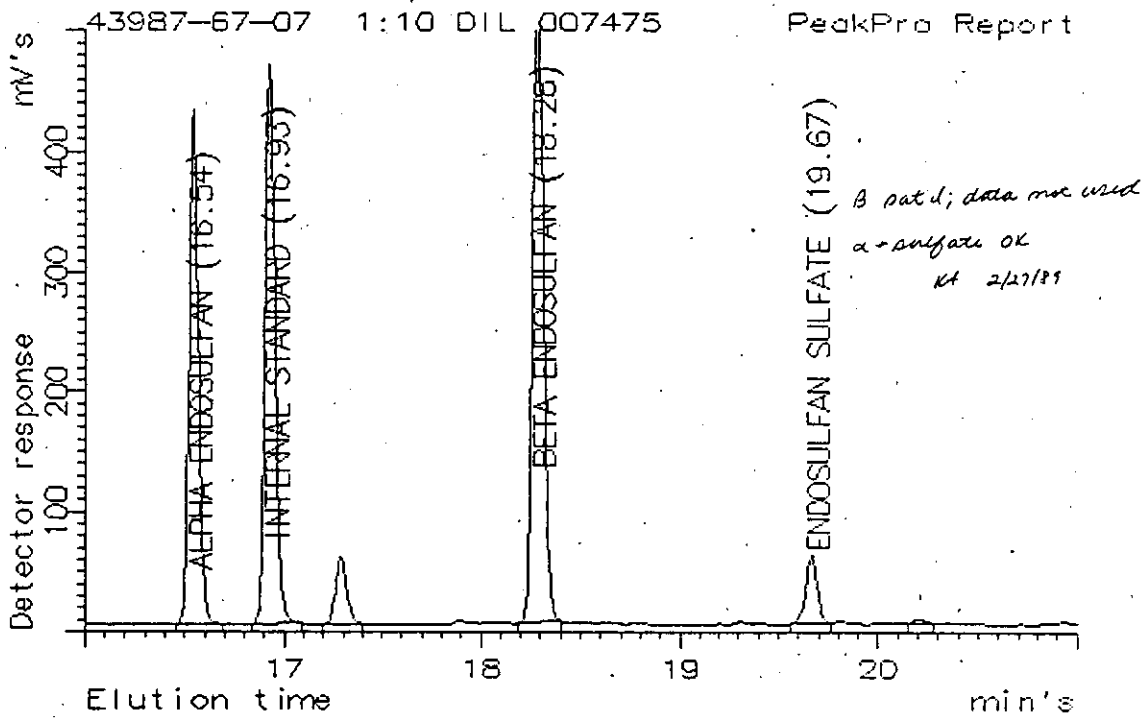
PeakPro CALIBRATION PLOT/REPORT 9:20:03 6/21/1989



Analysis method: 1190
Method Title: ENDOSULFAN COMPOUNDS - INSTRUMENT 19
Component Name: ENDOSULFAN SULFATE

Third degree polynomial fit
Polynomial Y = -0.0013 + 0.0015x + 0.0000x^2 - 0.0000x^3
RMS Deviation: 0.0009

	Calibration Level	NG/ML	Raw Values
1	STD 1	Not included in this level	
2	STD 2	5.000	0.0064
3	STD 3	10.000	0.0164
4	STD 4	25.000	0.0432
5	STD 5	50.000	0.1035
6	STD 6	100.000	0.2434
7	STD 7	250.000	0.6319



B patd; data not used
α-sulfate OK
KA 2/27/89

INTERNAL STANDARD HEIGHT ANALYSIS

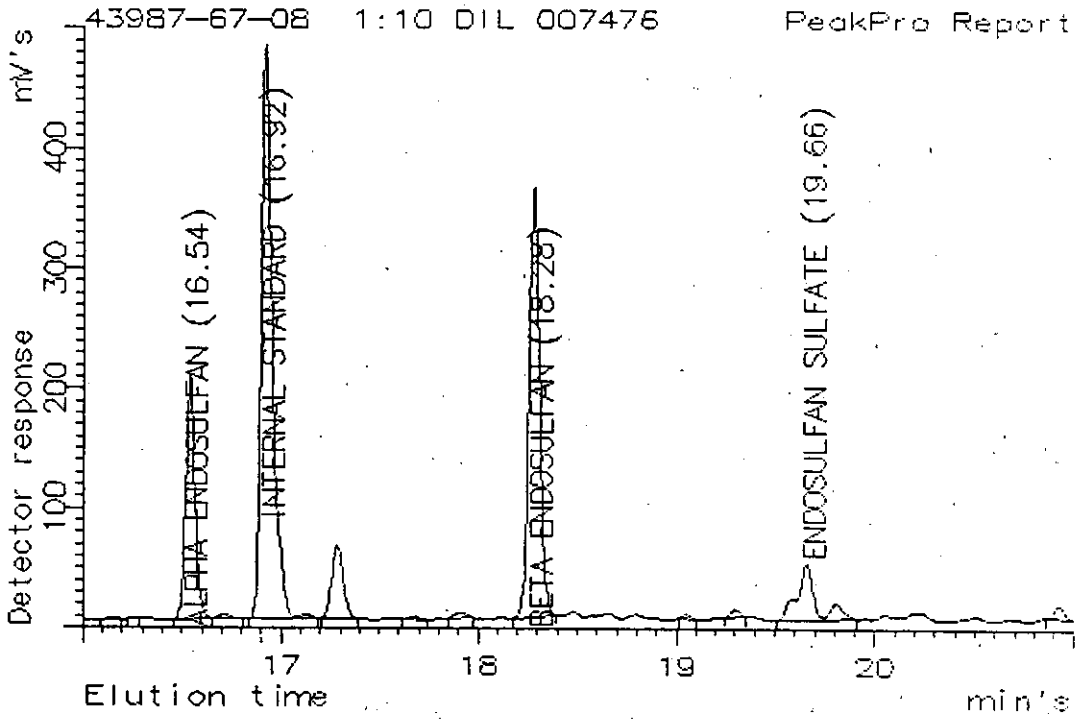
Acquisition Information:
Chromatogram: KN489 43987-67-07 1:10 DIL 007475 16:40:23 2/26/1989
AC Method: 1510 Inst 19 Vial # 0

Analysis Information:
AN Method: GC1520 43987-67-07 1:10 DIL 007475 8:29:23 2/27/1989
Analysis Method revision number: 57
Analyst: KIM ANDREWS Channel 0
Standard Weight: 2.0000 Factor 3: 50.0000
Sample Weight: 100.0000 Factor 4: 49.0000
[STANDARDxFACTOR3]/[SAMPLExFACTOR4] weight %: 2.0408

Testing Conditions
COLUMN: SPB-5 30 METER
OVEN: 60(1) - 220/20; 220 - 280/4

Component Name	RRT	RRF	PkNG/ML	Area	Height
ALPHA ENDOSULFAN	16.54	n/a	BCB 391.916	1404.871	421.628
INTERNAL STANDARD	16.93I	1.000	BCB	1623.115	459.310
BETA ENDOSULFAN	18.28	n/a	BCB-517.093	2037.629	546.351
ENDOSULFAN SULFATE	19.67	n/a	BCB 118.011	224.514	56.505

KA Mcy



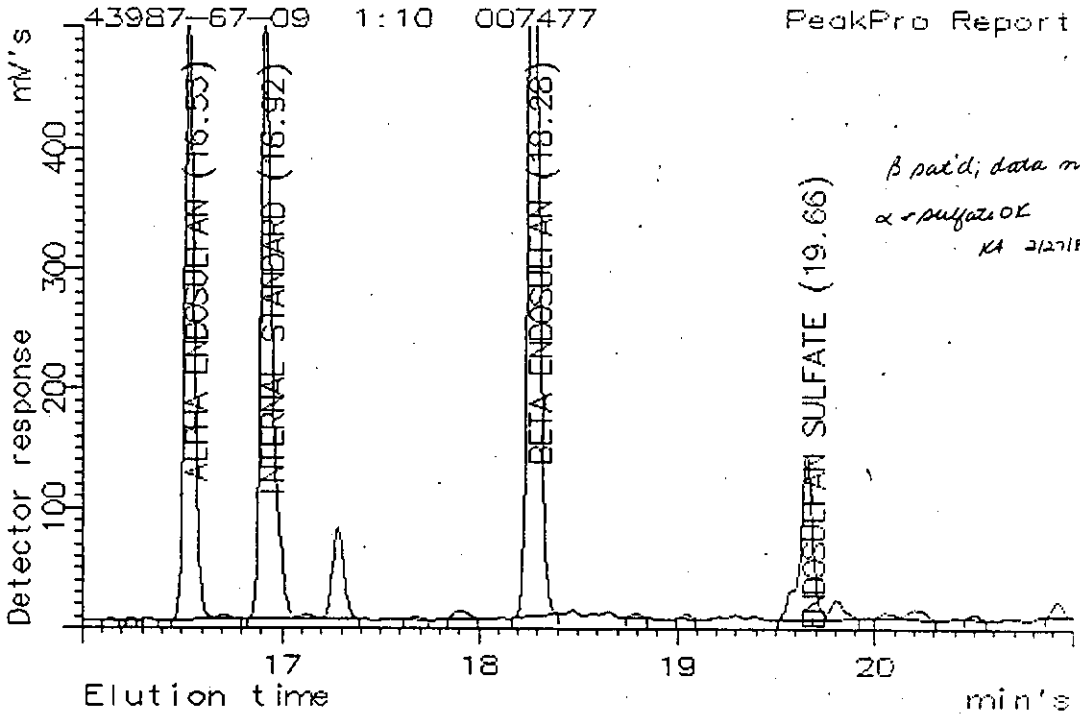
INTERNAL STANDARD HEIGHT ANALYSIS

Acquisition Information:
Chromatogram: KN490 43987-67-08 1:10 DIL 007476 17:09:36 2/28/1989
AC Method: 1510 Inst 19 Vial # 0

Analysis Information:
AN Method: GC1520 43987-67-08 1:10 DIL 007476 8:30:47 2/27/1989
Analysis Method revision number: 57
Analyst: KIM ANDREWS Channel 0
Standard Weight: 2.0000 Factor 3: 50.0000
Sample Weight: 100.0000 Factor 4: 49.0000
[STANDARDxFACTOR3]/[SAMPLExFACTOR4] weight %: 2.0408

Testing Conditions
COLUMN: SPB-5 30 METER
OVEN: 60(1) - 220/20; 220 - 280/4

Component Name	RRT	RRF	PkNG/ML	Area	Height
ALPHA ENDOSULFAN	16.54	n/a	BCB 187.586	664.605	200.612
INTERNAL STANDARD	16.92I	1.000	BCV	1854.437	471.945
BETA ENDOSULFAN	18.28	n/a	BCB 401.228	1316.397	353.370
ENDOSULFAN SULFATE	19.66	n/a	BCV 98.890	251.065	46.663



β paid; data not used
α - sulfate OK
KA 2/27/89

INTERNAL STANDARD HEIGHT ANALYSIS

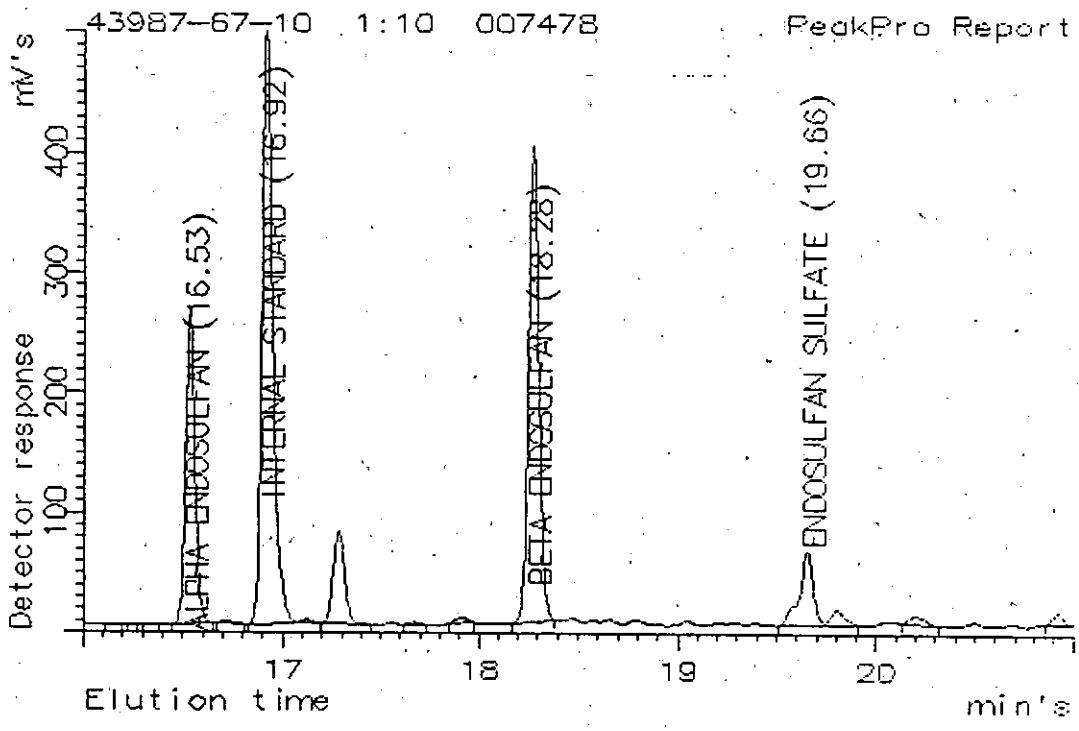
Acquisition Information:
Chromatogram: KN491 43987-67-08 1:10 DIL 007477 17:38:50 2/26/1989
AC Method: 1510 Inst 19 Vial # 0

Analysis Information:
AN Method: GC1520 43987-67-09 1:10 007477 8:31:45 2/27/1989
Analysis Method revision number: 57
Analyst: KIM ANDREWS Channel 0
Standard Weight: 2.0000 Factor 3: 50.0000
Sample Weight: 100.0000 Factor 4: 49.0000
[STANDARDxFACTOR3]/[SAMPLExFACTOR4] weight %: 2.0408

Testing Conditions
COLUMN: SPB-5 30 METER
OVEN: 60(1) - 220/20; 220 - 280/4

Component Name	RRT	RRF	PkNG/ML	Area	Height
ALPHA ENDOSULFAN	16.53	n/a	BCV 447.291	1716.409	506.929
INTERNAL STANDARD	16.92I	1.000	BCV	1934.828	491.257
BETA ENDOSULFAN	18.28	n/a	BCB-557.055	2760.488	733.667
ENDOSULFAN SULFATE	19.66	n/a	BCV 225.589	607.458	135.358

KA



INTERNAL STANDARD HEIGHT ANALYSIS

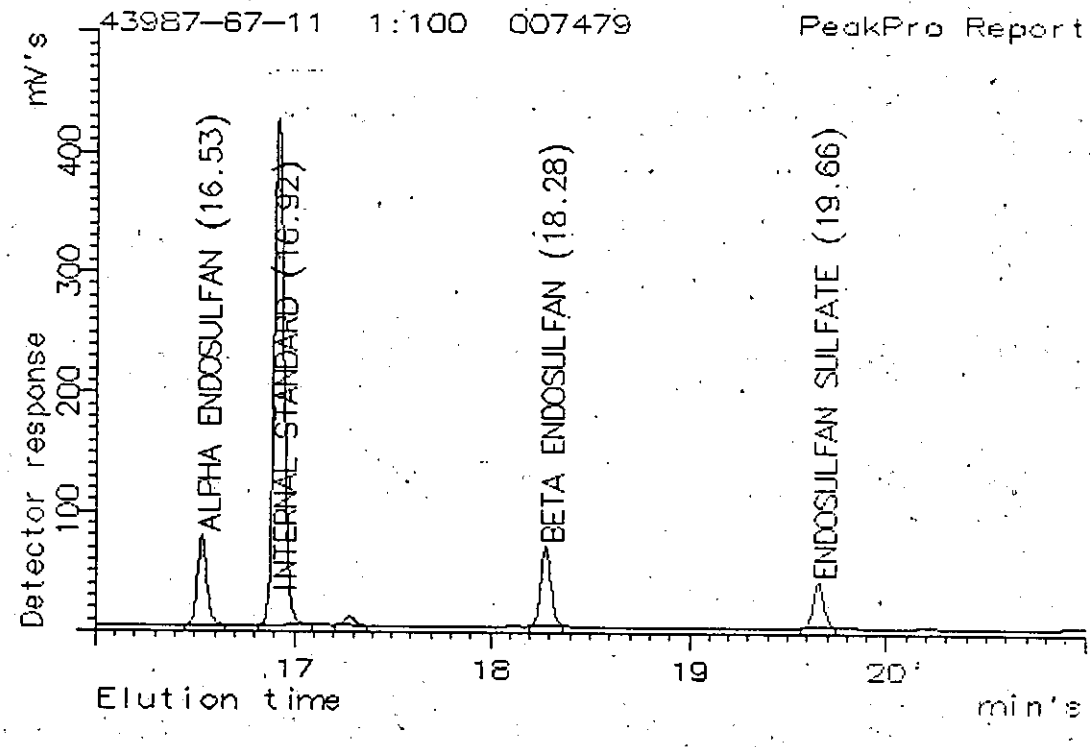
Acquisition Information:
Chromatogram: KN492 ~~43987-67-08 1:10 DIL 007478~~ error 18:08:05 2/24/1989
AC Method: 1510 Inst 19 Vial # 0

Analysis Information:
AN Method: GC1520 43987-67-10 1:10 007478 8:33:17 2/27/1989
Analysis Method revision number: 57
Analyst: KIM ANDREWS Channel 0
Standard Weight: 2.0000 Factor 3: 50.0000
Sample Weight: 100.0000 Factor 4: 50.0000
[STANDARDxFACTOR3]/[SAMPLExFACTOR4] weight %: 2.0000

Testing Conditions
COLUMN: SPB-5 30 METER
OVEN: 60(1) - 220/20; 220 - 280/4

Component Name	RRT	RRF	PkNG/ML	Area	Height
ALPHA ENDOSULFAN	16.53	n/a	BCB 224.921	859.814	261.585
INTERNAL STANDARD	16.92I	1.000	BCV	1846.253	492.592
BETA ENDOSULFAN	18.28	n/a	BCB 420.405	1445.555	393.266
ENDOSULFAN SULFATE	19.66	n/a	BCV 117.310	300.068	61.804

KA



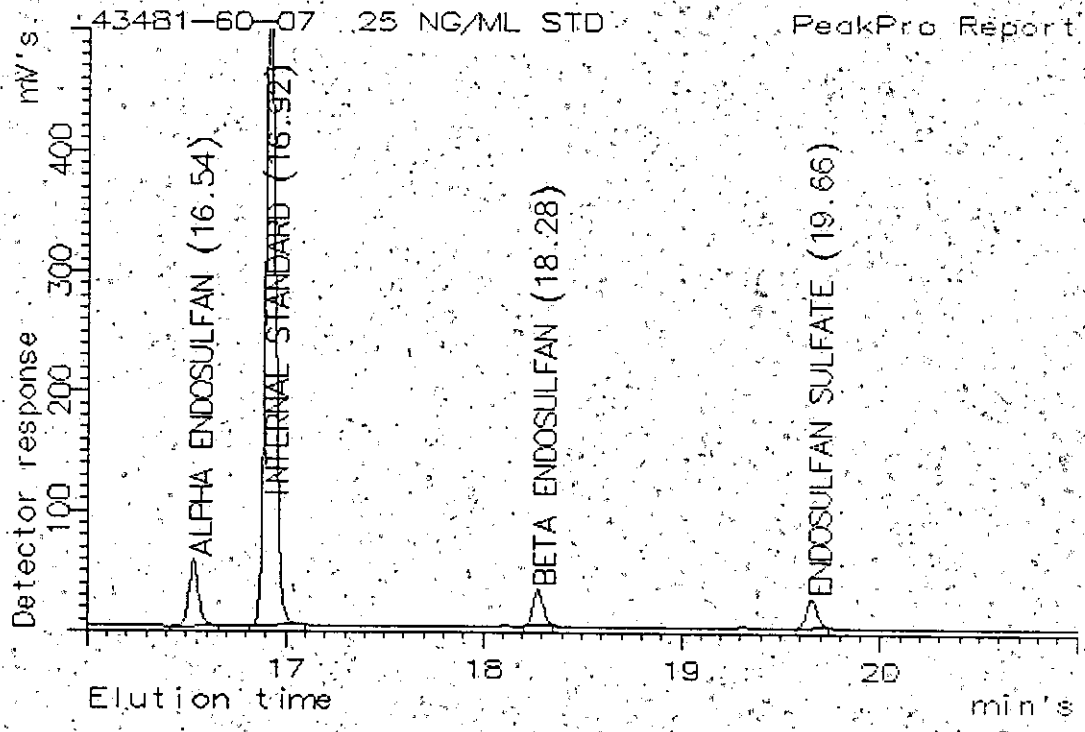
INTERNAL STANDARD HEIGHT ANALYSIS

Acquisition Information:
Chromatogram: KN493 ~~43987-67-09 1:100 DIL 007479~~ error 18:37:20 2/26/1989
AC Method: 1510 Inst 19 Vial # 0

Analysis Information:
AN Method: GC1520 43987-67-11 1:100 007479 8:34:31 2/27/1989
Analysis Method revision number: 57
Analyst: KIM ANDREWS Channel 0
Standard Weight: 2.0000 Factor 3: 500.0000
Sample Weight: 100.0000 Factor 4: 1000.0000
[STANDARDxFACTOR3]/[SAMPLExFACTOR4] weight %: 1.0000

Testing Conditions
COLUMN: SPB-5 30 METER
OVEN: 60(1) - 220/20; 220 - 280/4

Component Name	RRT	RRF	PkNG/ML		Area	Height
ALPHA ENDOSULFAN	16.53	n/a	BCB	42.070	247.702	74.553
INTERNAL STANDARD	16.92I	1.000	BCB		1467.062	415.775
BETA ENDOSULFAN	18.28	n/a	BCB	53.053	234.442	65.531
ENDOSULFAN SULFATE	19.66	n/a	BCB	43.729	137.041	36.246



INTERNAL STANDARD HEIGHT ANALYSIS

Acquisition Information:
Chromatogram: KN494 43481-60-07 25 NG/ML STD 19:06:33 2/26/1989
AC Method: 1510 Inst 19 Vial # 0

Analysis Information:
AN Method: GC1520 43481-60-07 25 NG/ML STD 8:35:40 2/27/1989
Analysis Method revision number: 57
Analyst: KIM ANDREWS Channel 0
Standard Weight: 1.0000 Factor 3: 1.0000
Sample Weight: 100.0000 Factor 4: 1.0000
[STANDARDxFACTOR3]/[SAMPLExFACTOR4] weight %: 1.0000

Testing Conditions
COLUMN: SPB-5 30 METER
OVEN: 60(1) - 220/20; 220 - 280/4

Component Name	RRT	RRF	PkNG/ML		Area	Height
ALPHA ENDOSULFAN	16.54	n/a	BCB	25.246	186.931	54.926
INTERNAL STANDARD	16.92I	1.000	BCB		1891.802	537.074
BETA ENDOSULFAN	18.28	n/a	BCB	22.143	106.860	29.375
ENDOSULFAN SULFATE	19.66	n/a	BCB	24.293	88.184	23.131
Total				71.682	381.976	107.432