Determination of Residues of Cloransulam-methyl in Soybeans and Soybean Forage, Hay, and Processed Commodities by Capillary Gas Chromatography with Mass Spectrometric Detection

Darcy D. Shackelford,* Dennis O. Duebelbeis, and Brian E. Snell

Global Environmental Chemistry Laboratories—Indianapolis Lab, DowElanco, 9330 Zionsville Road, Indianapolis, Indiana 46268

Cloransulam-methyl, *N*-(2-carbomethoxy-6-chlorophenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo[1,5-*c*]-pyrimidine-2-sulfonamide, is a new broad-spectrum herbicide for use in soybeans. The U.S. Environmental Protection Agency requires that analytical methodology be developed to enforce tolerance levels of pesticides in food crops. This paper describes the method developed to enforce tolerance levels of cloransulam-methyl in soybeans and soybean forage, hay, and processed commodities. The method description includes validation data supporting a lower limit of quantitation of 0.01 μg/g (10 ppb) for cloransulam-methyl in each matrix. Extracts of each matrix are purified using C_{18} and neutral alumina solid phase extraction. Cloransulam-methyl is derivatized, using (trimethylsilyl)diazomethane, to the *N*-methylcloransulam-methyl. Quantitation and simultaneous confirmation of residues of cloransulam-methyl as *N*-methylcloransulam-methyl employ gas chromatography with mass spectrometric detection using electron impact ionization with selected ion monitoring.

Keywords: *Cloransulam-methyl; sulfonamide; soybeans; (trimethylsilyl)diazomethane; GC/MSD*

INTRODUCTION

Cloransulam-methyl, *N*-(2-carbomethoxy-6-chlorophenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo[1,5-*c*]pyrimidine-2-sulfonamide, is a new DowElanco broad-spectrum, low-application-rate, low-toxicity herbicide which can be applied both pre- and postemergence for the control of many economically significant broadleaf weeds in soybeans. To support the registration of a pesticide for use on food crops, the U.S. Environmental Protection Agency (EPA) requires analytical methodology to enforce tolerance levels of the product in various food crop commodities. No previous methods are reported for the quantitative determination of residues of cloransulam-methyl in food crops. The analytical method described for soybean matrices employs capillary gas chromatography with mass spectrometric detection (GC/MSD) using electron impact ionization with selected ion monitoring. In addition to quantitation, the EPA requires all enforcement methods to include a confirmation technique. The use of GC/MSD allows for quantitation and simultaneous confirmation of cloransulam-methyl residues. Previous DowElanco methodology for the alkylation of sulfonamides prior to GC analysis has employed the use of diazomethane. Because of the hazards associated with the laboratory production of diazomethane, the EPA has banned the use of this reagent in enforcement methods. The use of (trimethylsilyl)diazomethane (TMSD), a stable and commercially available reagent, has been demonstrated as a substitute to diazomethane for alkylation of organic acids (Hashimoto et al., 1981). Although rapid and quantitative methylation of carboxylic acids is attained by the use of TMSD in methanol, quantitative methylation of the acidic sulfonamide nitrogen in cloransulam-methyl was found to require the addition of phosphoric acid.

EXPERIMENTAL PROCEDURES

Apparatus. *(a) Gas Chromatography with Mass Selective Detector (GC/MSD).* A Hewlett-Packard gas chromatograph, model 5890 Series II, with a model 5971A mass selective detector and model 7673A automatic sampler in combination with a model 486s/20 Vectra PC-based ChemStation and model G1034B data system software was used (Hewlett Packard, Wilmington, DE). The capillary column was a fused silica DB-5 liquid phase, 10 m × 0.18 mm i.d., 0.4-μm film thickness (J&W Scientific, Folsom, CA). A deactivated, cyclodouble-gooseneck, Restek catalog no. 20895-injection port liner (Restek, Bellefonte, PA) was used for splitless injection. The helium carrier gas had a linear velocity of approximately 50 cm/s. The column head pressure was approximately 45 kPa. The injector temperature was 300 °C, and the transfer line temperature was 310 °C. The GC oven was temperature-programmed from 120 °C (held for 1.1 min) to 325 °C at 20 °C/min (held for 2.0 min). The injection volume was 3 μL, and the purge time was set for 1.0 min. Under these conditions, the typical retention times were 9.89 and 10.06 min for *N*-methylcloransulam-methyl and *N*-ethylcloransulam-methyl (internal standard), respectively. The GC/MSD was operated using electron impact, in the selected ion-monitoring mode monitoring ions at *m/z* 166.0 (quantitation), 198.0 (confirmation of the analyte), and 212.0 (for the internal standard).

(b) Solid Phase Extraction (SPE) Cartridges. Neutral alumina and C_{18}, 1-g packing, SPE cartridges (Fisher Scientific, Pittsburgh, PA) were used for sample purification. Elution profiles were generated with standards on both neutral alumina and C_{18} cartridges to ensure adequate recoveries.

(c) Acrodisc Glass Fiber Filters. Acrodisc glass fiber filters (Gelman Sciences, Ann Arbor, MI) were used for sample filtration.

(d) Zymark TurboVap Evaporator. Zymark TurboVap (Zymark Corp., Hopkinton, MA) was used for large-scale sample evaporation.

(e) Reacti-Vap Evaporator. Reacti-Vap (Pierce Chemical Co., Rockford, IL) was used for small-scale sample evaporation.

(f) Omni Mixer Homogenizer. Omni mixer homogenizer (Omni International, Waterbury, CT) was used for sample blending during the extraction process.

(g) 40-mL Glass Vials. Screw-cap, glass vials, 40-mL, with PTFE-lined caps (Fisher Scientific) were used throughout sample purification.

Reagents. Solvents (acetone, acetonitrile, acetic acid, hexane, dichloromethane, and toluene) were all of HPLC grade

S0021-8561(96)00004-0 CCC: $12.00

or better and were purchased from EM Science, Gibbstown, NJ, or Fisher Scientific. Glacial acetic acid, 0.1 N hydrochloric acid, 0.5 N hydrochloric acid, 2 N hydrochloric acid, potassium dihydrogen phosphate, and 0.1 N sodium hydroxide were purchased from Fisher Scientific. Phosphoric acid and (trimethylsilyl)diazomethane (2 M in hexanes) were purchased from Aldrich Chemical Co., Milwaukee, WI. Analytical standards of cloransulam-methyl (*N*-(2-carbomethoxy-6-chlorophenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo[1,5-*c*]pyrimidine-2-sulfonamide), *N*-methylcloransulam-methyl (*N*-(2-carbomethoxy-6-chlorophenyl)-*N*-methyl-5-ethoxy-7-fluoro[1,2,4]triazolo[1,5-*c*]pyrimidine-2-sulfonamide), and *N*-ethylcloransulam-methyl (*N*-(2-carbomethoxy-6-chlorophenyl)-*N*-ethyl-5-ethoxy-7-fluoro-[1,2,4]triazolo[1,5-*c*]pyrimidine-2-sulfonamide) were obtained from DowElanco, Indianapolis, IN.

Safety Precautions. Each analyst should be acquainted with the potential hazards of the reagents, products, and solvents used in this method before commencing laboratory work. Safety information on the reagents and chemicals listed should be obtained from the suppliers in the form of material safety data sheets, literature, and other related data. Disposal of reagents, reactants, and solvents must be made in compliance with local, state, and federal laws and regulations. All extraction and evaporation steps should be performed in a well-ventilated fume hood away from ignition sources. Special precautions should be exercised in handling (trimethylsilyl)-diazomethane during derivatization, and work should be conducted in a well-ventilated fume hood. Protective gloves, proper eye protection, and protective clothing should be worn when working with these chemicals.

Internal Standard Preparation. A stock solution of *N*-ethylcloransulam-methyl was prepared at 1.0 mg/mL in acetone. An aliquot (5.0 mL) of the stock solution was quantitatively transferred to a 500-mL volumetric flask and diluted to volume with toluene to obtain a 10.0 μg/mL solution. An aliquot (40.0 mL) of the 10.0 μg/mL solution was quantitatively transferred to a 2000-mL volumetric flask and diluted to volume with toluene to obtain a 0.2 μg/mL solution for use in preparing the calibration standard solutions and diluting samples for analysis. Solutions of *N*-ethylcloransulam-methyl were stored in amber glass bottles with PTFE-lined caps as a precautionary measure even though they are quite stable under normal laboratory conditions.

Fortification Solution Preparation. A stock solution of cloransulam-methyl was prepared at 1.0 mg/mL in acetone. An aliquot (5.0 mL) of the stock solution was quantitatively transferred to a 500-mL volumetric flask and diluted to volume with acetone to obtain a 10.0 μg/mL solution. An aliquot (50.0 mL) of the 10.0 μg/mL solution was quantitatively transferred to a 500-mL volumetric flask and diluted to volume with acetone to obtain a 1.00 μg/mL solution. Additional fortification solutions were prepared to cover the validation range by further dilution with acetone of either the 1.00 or 10.0 μg/mL solutions to obtain solutions ranging from 0.10 to 5.00 μg/mL for use in fortifying control matrices for determination of analyte recovery. Solutions of cloransulam-methyl were stored in amber glass bottles with PTFE-lined caps as a precautionary measure even though they are quite stable under normal laboratory conditions.

Calibration Standard Preparation. A stock solution of *N*-methylcloransulam-methyl was prepared at 1.033 mg/mL in acetone (equivalent to 1.0 mg/mL cloransulam-methyl on a molar basis). An aliquot (5.0 mL) of the 1.033 mg/mL *N*-methylcloransulam-methyl stock solution and a 10.0-mL aliquot of the 10.0 μg/mL *N*-ethylcloransulam-methyl (internal standard) solution were both quantitatively transferred to a 500-mL volumetric flask and diluted to volume with toluene to obtain a 10.3 μg/mL solution (equivalent to 10.0 μg/mL cloransulammethyl) plus 0.2 μg/mL internal standard. An aliquot (20.0 mL) of the 10.3 μg/mL solution was quantitatively transferred to a 100-mL volumetric flask and diluted to volume with the 0.2 μg/mL internal standard solution in toluene to obtain a 2.06 μg/mL solution (equivalent to 2.00 μg/mL cloransulam-methyl). An aliquot (50.0 mL) of the 10.3 μg/mL solution (equivalent to 10.0 μg/mL cloransulam-methyl) was quantitatively transferred to a 500-mL volumetric flask and diluted to volume with the 0.2 μg/mL internal standard solution in toluene to obtain a 1.03 μg/mL solution (equivalent to 1.00 μg/mL cloransulam-methyl). Additional calibration standard solutions were prepared to cover the validation range by further dilution with the 0.2 μg/mL internal standard solution to obtain solutions of the analyte ranging from 0.01 to 1.00 μg/mL. Solutions of *N*-methylcloransulam-methyl were stored in amber glass bottles with PTFE-lined caps.

Sample Preparation and Determination of Cloransulam-methyl. *(a) In Soybeans and Soybean Forage, Hay, Meal, and Hulls.* Samples of soybeans and soybean forage, hay, meal, and hulls were ground thoroughly using a hammer mill, and 10.0-g portions were weighed into a series of 8-oz bottles equipped with PTFE-lined caps. Recovery samples were prepared by fortifying with 1.0 mL of the appropriate fortification standard solution to obtain concentrations ranging from 0.01 to 0.5 μg/g. Each sample received 100 mL of acetone/0.1 N hydrochloric acid (90:10) (v/v). Samples were blended at high speed for 1 min using an Omni mixer homogenizer. Sample bottles were capped, placed on a reciprocating shaker, and shaken at approximately 250 excursions/min for a minimum of 2 h. Extracted samples of soybeans and soybean forage, hay, meal, and hulls were centrifuged for 5 min at 2500 rpm, and 20-mL aliquots (2-g equiv) were quantitatively transferred, avoiding particulates, to 40-mL glass vials. The extracts were evaporated to dryness under nitrogen using a Zymark TurboVap with the water bath set at 60 °C. The dried residues then received 10 mL of 0.1 M potassium dihydrogen phosphate buffer (pH 7.5) and were solubilized by sonication and vortex mixing; 10 mL of hexane was added to each vial, and the contents were sonicated and vortex-mixed thoroughly. The samples were then centrifuged for 5 min at 2500 rpm, and the hexane layer was carefully removed with a disposable pipet and discarded. Any solids found at the interface were not removed. The sample vials were then placed under a stream of nitrogen on the TurboVap with the water bath set at 60 °C for approximately 10 min to evaporate any remaining hexane. Each sample received 2 mL of 2 N hydrochloric acid and was mixed by vortex action. Samples were allowed to stand for about 10 min until particulates coagulated and the aqueous portion was clear.

(b) In Soybean Crude and Refined Oil. For soybean crude and refined oil, 2.0-g samples were weighed into a series of 40-mL vials with PTFE-lined caps. Recovery samples were prepared by adding 200 μL of the appropriate fortification standard solution to obtain concentrations ranging from 0.01 to 0.50 μg/g. The samples were placed on the TurboVap at 60 °C under a stream of nitrogen for about 30 min to evaporate the acetone. Each sample received a 10-mL volume of hexane and was sonicated and vortex-mixed. An aliquot (10 mL) of 0.1 M potassium phosphate buffer (pH 7.5) was added to each sample which was sonicated and vortex-mixed. Samples were centrifuged for 5 min at 2500 rpm, and the hexane layer was carefully removed with a disposable pipet and discarded. A fresh 10-mL aliquot of hexane was added to each sample, and the sample was sonicated and vortex-mixed. The samples were again centrifuged for 5 min at 2500 rpm, and the hexane layer was removed and discarded. Vials were then placed on the TurboVap at 60 °C under a stream of nitrogen for about 10 min for evaporation of any remaining hexane. An aliquot (2 mL) of 2 N hydrochloric acid was added to each sample, and samples were vortex-mixed.

Sample Purification. *(a) By C_{18} Solid Phase Extraction.* Elution profiles of cloransulam-methyl were obtained on each new lot of C_{18} solid phase extraction (SPE) cartridges prior to purification to ensure optimum recovery and efficiency. Samples were purified using reversed phase C_{18} SPE cartridges which were first conditioned by rinsing with 5 mL of acetonitrile followed by rinsing with 5 mL of 0.5 N hydrochloric acid. The cartridges were not allowed to go to dryness. The acidified samples were added to the tops of the C_{18} SPE cartridges by slowly passing the extracts through an Acrodisc glass fiber filter attached to a 10-cc disposable syringe to remove suspended solids. With the aid of vacuum, the samples were pulled through the C_{18} SPE cartridges at a flow rate of 1−3 mL/min. The cartridges were rinsed with 10 mL of 80% 0.5

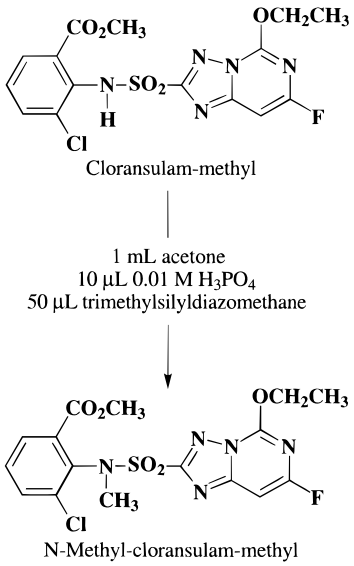

Figure 1. Derivatization of cloransulam-methyl with (trimethylsilyl)diazomethane.

N hydrochloric acid/20% acetonitrile at a flow of 1−3 mL/min, and the rinse was discarded. The C_{18} SPE cartridges were thoroughly dried by leaving them attached to the vacuum manifold and drawing air through them for at least 30 min or until the cartridges no longer were cold to the touch. As a final wash, the C_{18} cartridges were rinsed with 2 mL of hexane. The C_{18} cartridges were dried under vacuum for an additional 10 min with the rinse discarded. The cloransulam-methyl was then eluted with 5 mL of acetonitrile which was collected in a clean 3-dram vial.

(b) By Neutral Alumina Solid Phase Extraction. Elution profiles of cloransulam-methyl were obtained on each new lot of neutral alumina SPE cartridges prior to purification to ensure optimum recovery and efficiency. Samples were further purified with neutral alumina SPE cartridges which were preconditioned by rinsing with 5 mL of acetonitrile. The acetonitrile eluants from the C_{18} SPE cartridges were quantitatively transferred to the top of each alumina SPE cartridge and drawn through the cartridges at a flow rate of 1−3 mL/min. The alumina SPE cartridges were rinsed with 5 mL of acetonitrile and then dried for approximately 15 min under vacuum. The alumina SPE cartridges were washed with 4.0 mL of 99.5% dichloromethane/0.5% acetic acid using care to avoid drying of the column, and the wash was discarded. The cloransulam-methyl was then eluted from each cartridge into a clean 3-dram vial with 8 mL of 99.5% dichloromethane/0.5% acetic acid at a flow rate of approximately 1−3 mL/min. The eluant was then evaporated to complete dryness under a stream of nitrogen using a dry bath set at 60 °C.

Sample Derivatization. Samples were prepared for derivatization by adding 1.0 mL of acetone, 10 μL of 0.01 M phosphoric acid solution (in acetone), and 50 μL of (trimethylsilyl)diazomethane (TMSD; 2 M in hexanes) to each vial. Samples were sealed with PTFE-lined caps, vortex-mixed for 10−15 s and allowed to react at ambient temperature for 30 min. Derivatized samples were then placed under a stream of nitrogen on a dry bath set at 60 °C for complete evaporation of all solvents; 4 mL of deionized water was added to each sample vial, and the samples were sonicated and vortex-mixed. Finally 1.0 mL of toluene containing 0.2 μg/mL *N*-ethylcloransulam-methyl as an internal standard was added to each vial, and the samples were sonicated and vortex-mixed. The samples were centrifuged for 5 min at 2500 rpm. A portion of the toluene layer was carefully drawn off so as not to pick up any water and placed in a 2-mL autoinjector vial containing a 250-μL glass insert. The vials were sealed with a cap using a crimper prior to analysis by gas chromatography with mass selective detection. A typical analytical set consisted of a minimum of five standards encompassing the expected range of the gross sample concentrations, a reagent blank, a control

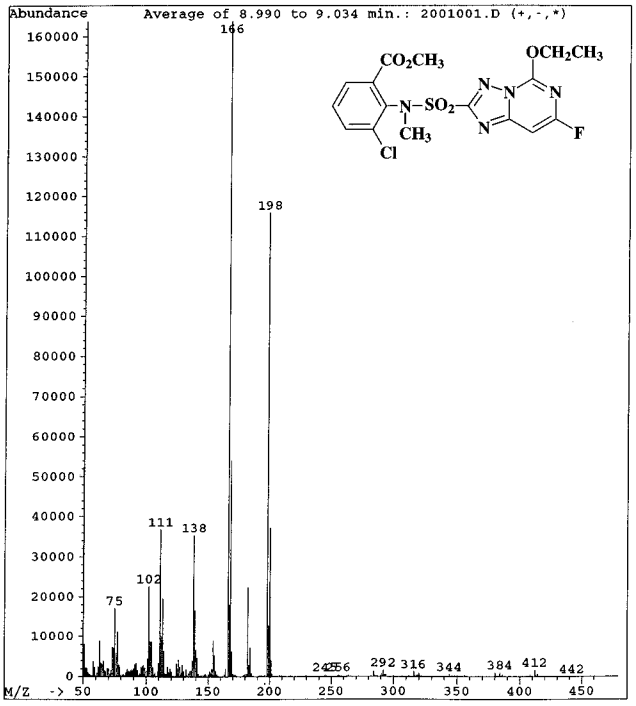

Figure 2. Full scan mass spectrum of *N*-methylcloransulam-methyl (MW 443).

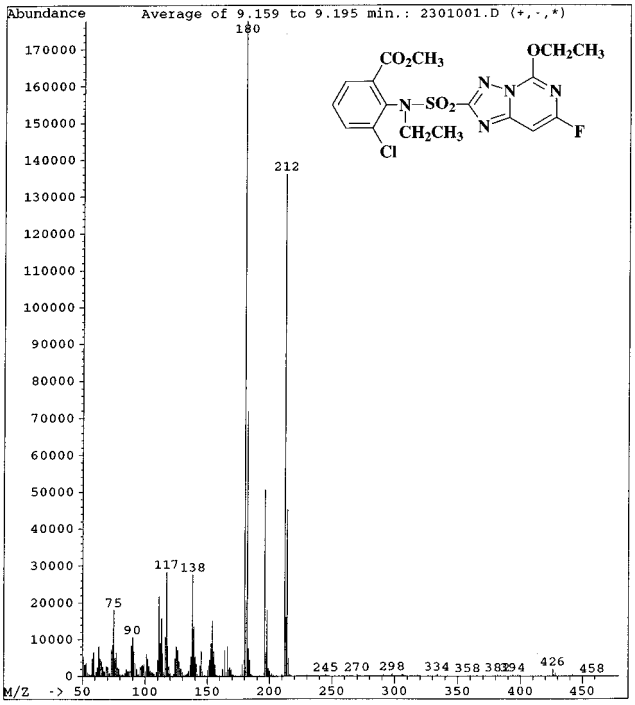

Figure 3. Full scan mass spectrum of *N*-ethylcloransulam-methyl (MW 457).

(a nonfortified sample), a minimum of two fortified controls (one of which was fortified at the limit of quantitation), and 14 samples. Typically, calibration standards were injected both before and after the sample set.

Chromatography. Some precautions were required to preserve adequate chromatographic representation. The inlet liner was replaced, and approximately 10 cm of the head of the gas chromatographic column was removed when sensitivity became inadequate for the lowest standard of interest.

Calculation of Results. Integration of the peak areas was performed by the GC/MSD data system software. The area of the analyte peak (*m*/*z* 166 for *N*-methylcloransulam-methyl) divided by the area of the internal standard peak (*m*/*z* 212)

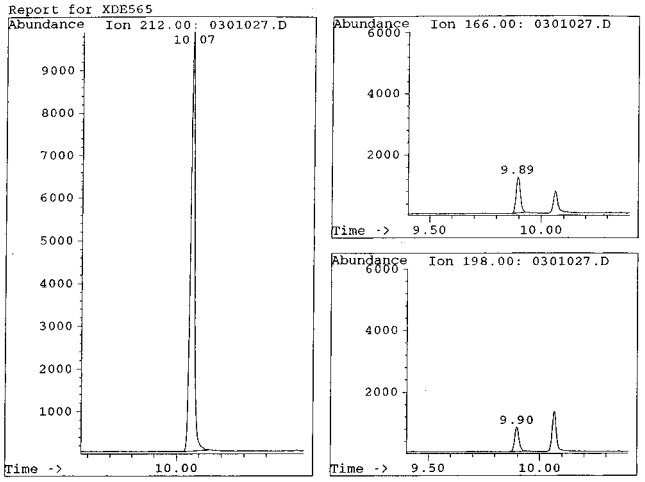

Figure 4. Representative chromatogram of cloransulam-methyl: standard, 0.02 μg/mL cloransulam-methyl; retention time internal standard, 10.07 min; retention time *N*-methyl-cloransulam-methyl, 9.89 min.

gave quantitation ratios. Power regression analysis of the standard curve data was performed, and recoveries of the fortified control samples were calculated from the standard curve (Hewlett-Packard, 1982). The correlation coefficient (r^2) for the power regression analysis describing the detector response as a function of the standard calibration curve over the concentration range of 0.01−2.00 μg/mL was greater than 0.99 for each validation set.

The power regression equation is as follows (eqs 1 and 2):

$$Y = \text{constant} \times X^{(\text{exponent})} \quad (1)$$

$$X = \left(\frac{Y}{\text{constant}}\right)^{1/\text{exponent}} \quad (2)$$

where X is the analyte concentration (μg/mL), and Y is the quantitation ratio (eq 3)

$$\text{cloransulam-methyl conctn } (\mu\text{g/mL}) = \left(\frac{\text{166/212 peak area ratio}}{\text{constant}}\right)^{1/\text{exponent}} \quad (3)$$

To calculate μg/g found (eq 4):

$$\text{cloransulam-methyl conctn } (\mu\text{g/g}) = \left(\frac{\mu\text{g/mL} \times 1.00 \text{ mL (final vol)}}{\text{2.0-g equiv of sample wt}}\right) \quad (4)$$

The percent recovery was determined by dividing the concentration found for each recovery sample by the theoretical concentration added and multiplying by 100 (eq 5):

$$\text{cloransulam-methyl \% recovery} = \left(\frac{\text{conctn found}}{\text{conctn added}}\right) \times 100 \quad (5)$$

The cloransulam-methyl concentration in the samples was corrected for percent recovery as follows (eq 6):

$$\text{chloransulam-methyl conctn (corrected mg/}\mu\text{L)} = \text{cloransulam-methyl conctn } (\mu\text{g/g}) \times \left(\frac{100}{\text{\% recovery}}\right) \quad (6)$$

Confirmation of Residue Identity. Confirmation ratios were used to determine whether or not peaks detected at the retention times of the analyte were in fact cloransulam-methyl. The peak area ratios of ion m/z 198 divided by m/z 166 were calculated for each calibration standard and sample injected. If the ion ratio was not within the established limits of ±10% of the average found for the calibration standards, the identity of a detected peak was not considered confirmed as the analyte.

RESULTS AND DISCUSSION

Cloransulam-methyl required derivatization prior to GC/MSD analysis and was readily and quantitatively *N*-methylated using (trimethylsilyl)diazomethane as depicted in Figure 1. The resulting mass spectra of *N*-methyl- and *N*-ethylcloransulam-methyl are shown in Figures 2 and 3, respectively.

Chromatograms shown in Figures 4 and 5 depict a typical standard, control, and fortified soybean sample analyzed for cloransulam-methyl. Only chromatograms of control and fortified soybean samples are shown since other soybean matrices typically looked the same. Each chromatogram consists of three selected ion abundance tracings including the m/z 198 quantitation, 166 confirmation, and 212 internal standard ions.

Validation of the method involved fortification of samples over a concentration range of 0.01−0.50 μg/g used for the validation of the procedure. Recovery and precision data were summarized for each soybean

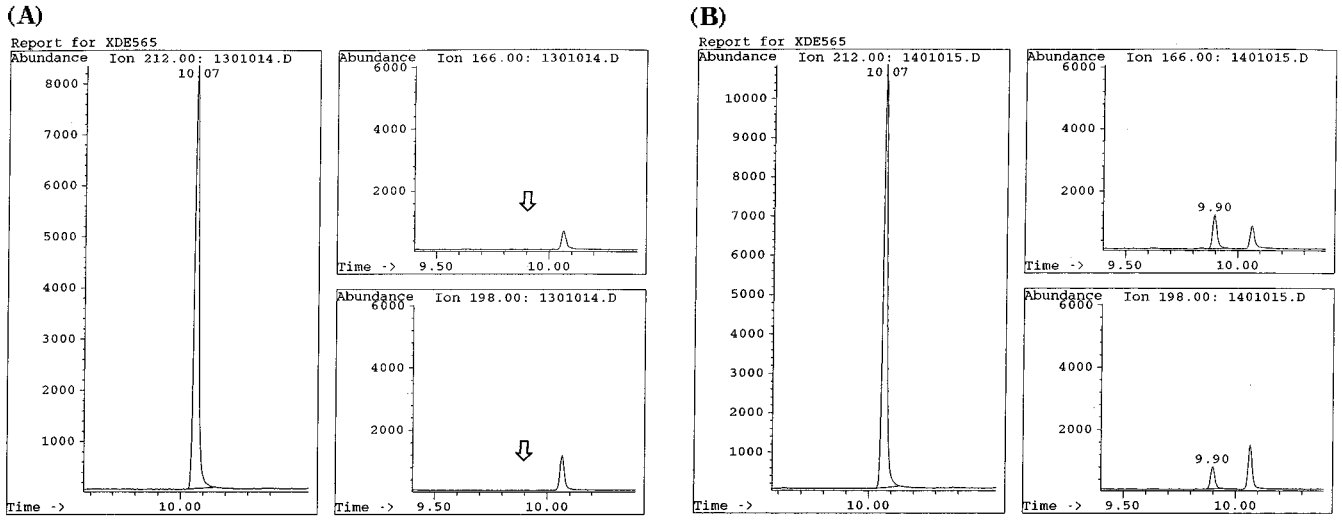

Figure 5. Representative chromatograms of cloransulam-methyl: (A) 2.0-g equiv of control soybean grain and (B) 2.0-g equiv of control soybean sample fortified with 0.01 μg/g cloransulam-methyl; retention time internal standard, 10.07 min; retention time *N*-methylcloransulam-methyl, 9.89 min.

Table 1. Recovery of Cloransulam-methyl from Soybean Matrices

matrix	fortification level, μg/g	*n*	% recovery mean	% recovery SD	matrix	fortification level, μg/g	*n*	% recovery mean	% recovery SD
soybeans	0.01	9	90		hulls	0.01	8	98	
	0.025	2	81						
	0.025	2	96						
	0.05	2	82						
	0.05	2	100						
	0.10	2	83						
	0.10	2	100						
	0.25	2	79						
	0.25	2	96						
	0.50	2	75						
	0.50	2	93						
overall		19	85	6	overall		18	97	3
forage	0.01	9	87		crude oil	0.01	8	101	
	0.025	2	96						
	0.025	2	97						
	0.05	2	86						
	0.05	2	98						
	0.10	2	87						
	0.10	2	95						
	0.25	2	84						
	0.25	2	93						
	0.50	1	82						
	0.50	2	88						
overall		18	87	7	overall		18	97	6
hay	0.01	8	93		refined oil	0.01	8	99	
	0.025	2	96						
	0.025	2	103						
	0.05	2	97						
	0.05	2	104						
	0.10	2	89						
	0.10	2	103						
	0.25	2	76						
	0.25	2	102						
	0.50	2	77						
	0.50	2	99						
overall		18	89	9	overall		18	100	3
meal	0.01	8	100						
	0.025	2	85						
	0.05	2	89						
	0.10	2	81						
	0.25	2	72						
	0.50	1	76						
overall		17	90	11					

matrix at each fortification level (Table 1). In addition, extraction efficiency studies were conducted to evaluate the extraction of field-incurred residues of cloransulam-methyl on soybeans treated with [^{14}C]cloransulam-methyl both pre- and postemergence (Stafford et al., 1995; Lewer et al., 1995). Levels of ingrown residues of cloransulam-methyl in forage from postemergence treatment were determined by GC/MSD. The values determined by this method agreed closely with those found by ^{14}C-quantitation techniques, providing additional method validation support. A study was conducted to determine the potential for interference to the method resulting from other pesticides used on soybeans. A total of 47 pesticides were analyzed by GC/MSD operating in the electron impact full-scan mode using the conditions described in the method for determination of cloransulam-methyl. Detector response was monitored for ions over the range of m/z 50−550, and the retention times and mass spectra of the compounds were compared to that of cloransulam-methyl. None of the 47 compounds studied were found to interfere with the determination of cloransulam-methyl (Knapp et al., 1996).

Limits of quantitation (LOQ) and detection (LOD) were calculated following a published technique (Keith et al., 1983). By this technique, the LOD was calculated as 3 times the standard deviation of the concentrations found at the lowest recovery level (the targeted LOQ), and the LOQ was calculated as 10 times the standard deviation of the concentrations found (Table 2). The calculated LOD and LOQ were lower than the validated limits for each matrix; however, numerical values for residues found at levels below the validated LOQ were not reported.

Table 2. Calculated Limits of Detection and Quantitation for Cloransulam-methyl in Soybean Matrices

		μg/g cloransulam-methyl			
		concentration found		calculated LOD/LOQ	
matrix	*n*	mean[a]	SD[b]	LOD = 3SD	LOQ = 10SD
soybeans	9	0.0090	0.0002	0.0006	0.0021
forage	9	0.0087	0.0009	0.0026	0.0086
hay	9	0.0093	0.0006	0.0018	0.0060
meal	8	0.0100	0.0004	0.0012	0.0039
hulls	8	0.0098	0.0002	0.0005	0.0017
crude oil	8	0.0101	0.0006	0.0017	0.0058
refined oil	8	0.0099	0.0003	0.0008	0.0026

[a] Mean of concentrations found for samples fortified at 0.01 μg/g cloransulam-methyl. [b] Standard deviation (SD) of concentrations found for samples fortified at 0.01 μg/g cloransulam-methyl.

The data presented in this paper demonstrate the suitability of this method for the determination of residues of cloransulam-methyl in soybeans and soybean forage, hay, meal, hulls, and crude and refined oil, with validated LOD and LOQ values of 0.003 and 0.01 μg/g,

respectively. Recovery of cloransulam-methyl was achieved by solvent extraction and further purification by physical and chemical separations. The derivatization reaction produced *N*-methylcloransulam-methyl, which was a thermally stable product, easily quantifiable by GC/MSD. This method has been used successfully to analyze samples of soybean raw agricultural products (soybeans and soybean forage and hay, respectively) and processed commodities (soybean meal, hulls, and crude and refined oil). Selectivity and sensitivity were sufficient to reliably measure cloransulam-methyl below the proposed tolerance levels of 0.02, 0.1, and 0.2 μg/g in soybean raw agricultural products (soybeans and soybean forage and hay, respectively). No tolerances were proposed for soybean processed fractions since no residues were found at or above the LOD of the method.

LITERATURE CITED

Hashimoto, N.; Aoyama, T.; Hioiri, T. *Chem. Pharm. Bull.* **1981**, *29* (5), 1475−1478.

Hewlett-Packard. Hewlett-Packard Publication 00041-90402. *HP-41C/41 CV Standard Applications Handbook;* Hewlett-Packard: Wilmington, DE, 1982; pp 42−48.

Keith, L. H.; Crummett, W.; Deegan, J.; Libby, R. A.; Taylor, J. K.; Wentler, G. Principles of environmental analysis. *Anal. Chem.* **1983**, *55*, 2210−2218.

Knapp, C. M.; Shackelford, D. D. DowElanco. Unpublished results, 1996.

Lewer, P.; Finney-Brink, K. L. DowElanco. Unpublished results, 1995.

Stafford, L. E.; Lardie, T. S.; Brink, D. L. DowElanco. Unpublished results, 1995.

Received for review January 2, 1996. Revised manuscript received July 11, 1996. Accepted July 26, 1996.[⊗]

JF960004G

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1996.