FMC Agricultural Chemical Group
Princeton

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COMMAND

Title: METHOD FOR DETERMINATION OF FMC 57020 RESIDUES IN/ON SOYBEANS

Project No. and Title: G164 - FMC 57020 Herbicide

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ABSTRACT

The FMC 57020 residue method for soybeans included an acid hydrolysis, hexane extraction, a sodium bicarbonate wash and cleanup by Forisil® column. FMC 57020 residues was quantitated by gas chromatographic-mass spectrometry (GC/MS) in the selected ion monitoring mode. Method sensitivity for FMC 57020 in soybeans was established as 0.05 and method detectability at 0.01 ppm. Average method recovery and standard deviation was 87 ± 11%.

FMC Authorizes EPA to release, publish or otherwise use as required for establishment of the FMC 57020 tolerances.

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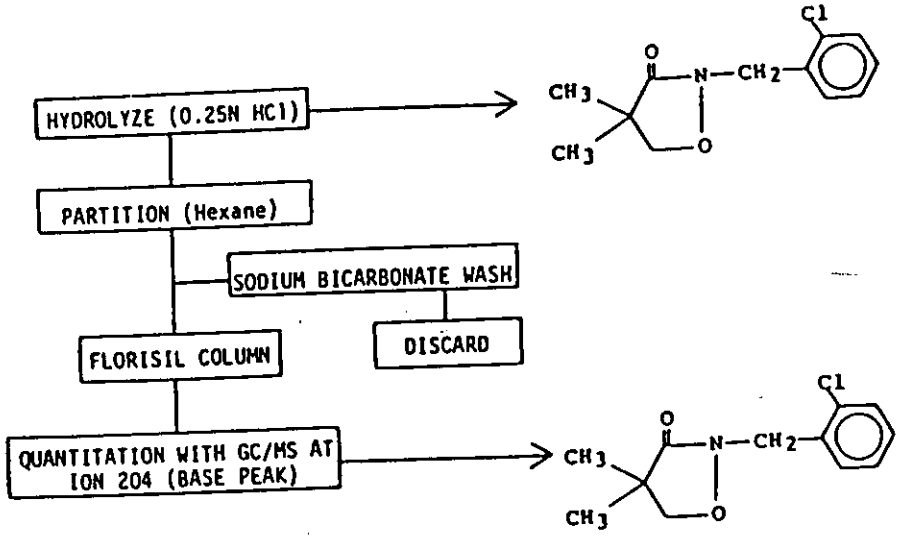
I. ANALYTICAL METHOD

The soybean samples were acid hydrolyzed. FMC 57020 residues were recovered from acid hydrolysate by hexane extraction. The hexane solution was washed with sodium bicarbonate solution and then evaporated to a small volume for addition to a Florisil column cleanup. The sample extract was quantitated using gas chromatograhy-mass spectrometry (GC/MS) in a selected ion monitoring mode. Figure 1 presents that method flow scheme.

FIGURE 1

FMC 57020 FLOW CHART
SOYBEAN METHOD



A. Apparatus

Condenser, 200 mm and 300 mm jacket with 24/40 ȝ inner drip
Flask, Erlenmeyer, 125, 250 ml
Flask, round-bottom, 1000 ml with 50/50 ȝ neck opening and a 50/50 ȝ to 24/40 ȝ neck reducing adapter
Funnel, glass 4" diameter
Funnel, separatory, 1000 ml
Graduated cylinder, 10, 50, 100, 500, 1000, 2000 ml
Heating mantle, hemispherical, 1000 ml with variac power control
Hobart® food chopper with coffee grinding attachment
Kuderna-Danish evaporative concentrator, 1000 ml with a 24/40 ȝ top joint and a 24/25 ȝ bottom joint and retaining hooks
Magnetic stirring bar and power control
N-EVAP® evaporator
Snyder column, 3 ball, 250 mm
Steam bath
Syringe, Hamilton, 10, 25, 50, 100 µl
Turbomatic Jr. glassware washer, series 7000, Better-Built Machinery Corp.

B. Instrumentation

Gas chromatograph-mass spectrometer Hewlett-Packard 5992.

GC column, 122 cm x 2 mm (I.D.) glass silanized with Sylon-CT reagent. Packed with 5% OV-3 on Chromosorb W HP 80/100 mesh (Supelco) using suction and a vibrator.

C. Reagents

Distilled water (house still)
Filter paper, fluted 515
Florisil® 100/200 mesh, Floridin Co. (3% H_2O)
Glass wool, fiber, Pyrex, Corning Glass Works
Hexane, Resi-Analyzed, Baker
Hydrochloric acid, concentrated, V.W.R.
Sodium bicarbonate, saturated aqueous solution
Versatone®, glassware cleaning agent, V.W.R.

D. Procedures

1. Acid Hydrolysis

Five grams of soybeans were acid hydrolyzed by refluxing for one hour in a 1000 ml round-bottom flask containing 250 ml of 0.25N HCl. The acid solution was allowed to cool overnight at room temperature. The mixture was filtered through glass wool and the flask was rinsed with ~130 ml HCl (0.25N). The volume was adjusted to 400 ml with 0.25N HCl and 200 ml aliquot was used for extraction.

2. Extraction

The FMC 57020 residues were extracted from the aqueous solution three times with 200 ml of hexane after the addition of (4 ml) 4% sodium lauryl sulfate solution to break emulsions. The hexane was washed with 100 ml of saturated sodium bicarbonate. The hexane extract was then transferred to a 1000 ml Kuderna-Danish evaporator and evaporated to about 10 ml. The 10 ml hexane was further evaporated to ~2 ml using an N-EVAP® under nitrogen.

3. Florisil Column Cleanup

The Florisil column was prepared by filling a 15 mm I.D. glass column with about 100 ml hexane. Ten grams of 3% water-deactivated Florisil was slowly added. The hexane was drained to about 1/4 inches above the Florisil packing. The residual extract of hexane (2 ml) was transferred quantitatively to the Florisil column and the containing tube was washed with 2 x 2 ml of hexane and transferred successively to the column. The column was eluted with 100 ml of 5% ethyl acetate in hexane. This eluant was discarded. The column was further eluted with 100 ml of 10% ethyl acetate in hexane. This eluant contains FMC 57020, which was transferred to a 500 ml Kuderna Danish evaporator and evaporated to about 10 ml. This hexane solution was further evaporated using an N-EVAP® to about 5 ml. This extract was transferred to a 12 ml centrifuge tube and evaporated by N-EVAP® to <1 ml. The hexane solution was adjusted to 1.0 ml for GC/MS analysis.

E. Analysis

FMC 57020 was quantitated using a Hewlett-Packard 5992 gas chromatograph-mass spectrometer at FMC 57020 base peak (ion 204).

Column Parameters:

Length:	122 cm (glass)
Diameter:	2 mm I.D.
Packing:	5% OV-3 on Chromosorb W HP 80/100 mesh
Injection Port Temperature:	240°
Column Temperature:	180°C
Carrier Gas:	He at 25 ml/min

Typical Parameters for Mass Spectrometer:

Repeller:	255
Ion Focus:	0
E.M. Volts:	1800
Gain:	141
Offset:	47
Entrance Lens:	48
X-ray:	95

II. QUANTITATION

The samples were injected and a standard injection (0.5 ng in hexane) was made after two sample injections. The resulting three or four standards were averaged and the average value used to calculate residue values.

The following formula was used for quantitation:

$$\text{ppm} = \frac{\text{Area unknown x ng standard}}{\text{Average area of standard x mg crop injected}}$$

All residue values (ppm) were corrected for average method recovery.

III. ANALYTICAL LIMITS

Method sensitivity, or the quantitatively reliable measurement of response, was validated to 0.05 ppm by successful recovery from fortified soybeans. Method detectability (i.e., recognition of responses) was possible when the area of the peaks of interest exceeded about 200 area counts. This represents approximately 0.01 ppm of FMC 57020. Any response below this value was considered non-detectable (ND).

IV. FORTIFICATION RECOVERIES

A. Standard Preparation

The following standards were used for fortification and chromatographic standards.

Compound	Reference No.	Concentration	Solvent
FMC 57020	E1376-148D	0.01 µg/µl	hexane
FMC 57020	E1376-148D	0.25 Ng/µl	hexane

B. Fortification

Untreated (check) samples were fortified prior to any analytical manipulation. The recovery results are summarized in Table I.

TABLE I

RECOVERY OF FMC 57020 FROM FORTIFIED SOYBEAN SAMPLES

Check Sample Identification	Fortification Level (ppm)	Recovery Level	
		ppm	%
PR2-29-RAK82-29A-36A	0.10	0.085	85
MRY-634-82-TRW-13 + 14A	0.05	0.055	110
MRY-587-82-RSP-27-30A	0.05	0.039	78
MRY-640-82-CRF-96A	0.05	0.045	90
MRY-606-82-MTH-34A	0.05	0.049	98
MRY-657-WSH-82-20A-27A	0.05	0.044	88
MRY-615-82-DRR-65A	0.05	0.041	82
MRY-682-AEP-82-141A-146A	0.05	0.046	92
MRY-683-AEP-82-147A-150A	0.05	0.042	84
MRY-614-LJW-82-125A	0.05	0.035	70
MRY-592-REC-04-82-131	0.05	0.039	78
			87 ± 11

V. CHROMATOGRAMS

FIGURE 2

TYPICAL STANDARD INJECTION (FMC 57020)
(AVERAGE AREA COUNTS FOR 0.5 ng STANDARD INJECTION IS 3692)

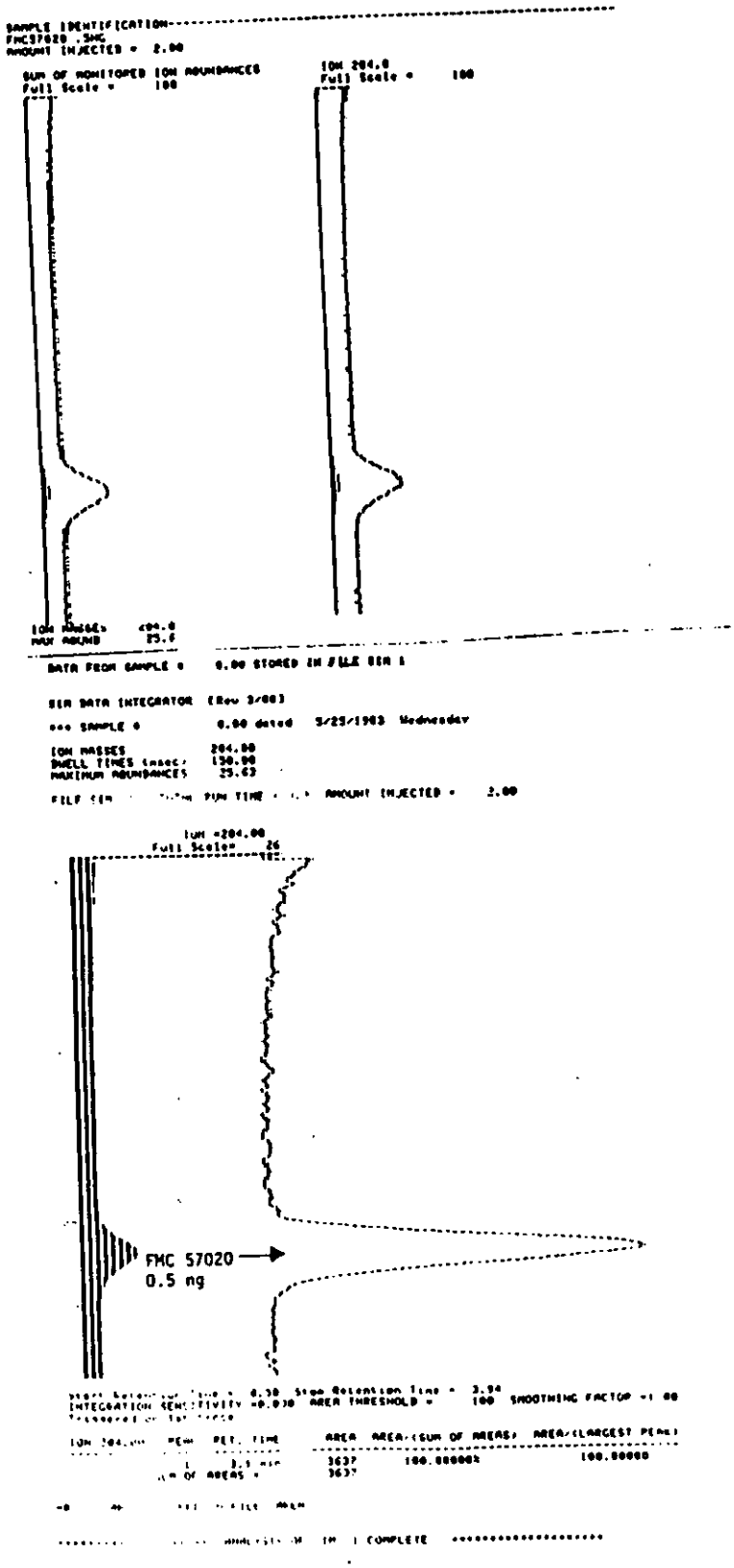


FIGURE 3

UNTREATED SOYBEANS
CHECK SAMPLE NO. MRY-606-82-MTH-34A, 5 MG INJECTED

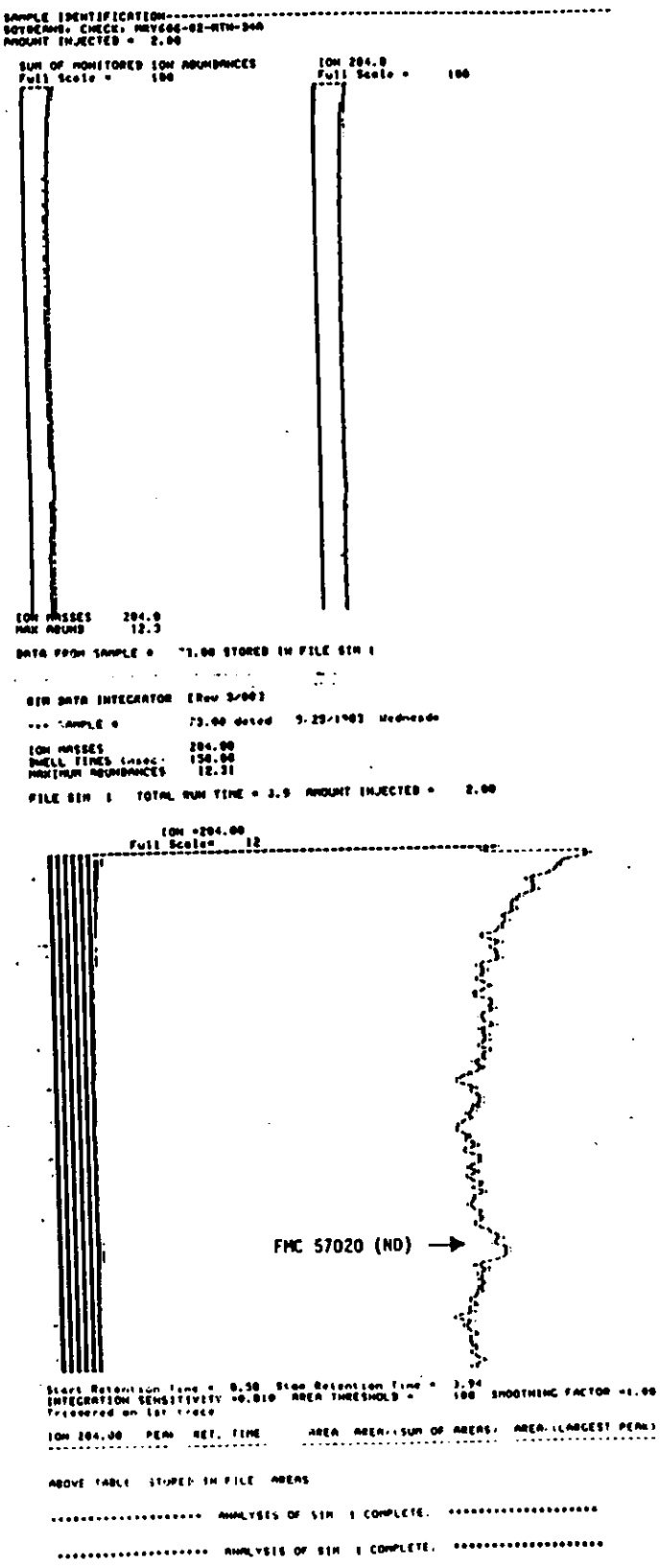


FIGURE 4

FORTIFIED UNTREATED SOYBEANS
CHECK SAMPLE NO. MRY-606-82-MTH-34A FORTIFIED WITH 0.05 PPM, 5 MG INJECTED