US EPA ARCHIVE DOCUMENT

RAVEN Systems & Research Inc.
Filmed by: J. Herrington 5/14/80

DETERMINATION OF LINURON RESIDUES ON ASPARAGUS

STATE OF CALIFORNIA
DEPARTMENT OF FOOD AND AGRICULTURE

Validate

00041-025-10
293663-3-C

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ANALYTICAL METHOD

SCOPE

This method in the form outlined is to be used only for linuron residues in or on asparagus.

SUMMARY

The linuron is separated from the asparagus by extraction with benzene. Interfering materials are removed by chromatographing with Florisil. Detection and quantitative determination of the linuron is carried out with a gas-liquid chromatograph equipped with a Coulson Conductametric Nitrogen Detector. (HALL)

EQUIPMENT AND REAGENTS

EQUIPMENT

Gas Chromatography - Varian Aerograph 2100

Column - 3% OV-101 on 100/120 Vavaport 30 packed in a 6 ft. by 1/8 in. ID Pyrex column.

Hobart Salad Maker or equivalent

Syringe - Hamilton No. 701 or equivalent

Chromatographic Tube - 20 mm. ID Pyrex

Blender - Omnimixer or similar design

Misc. Laboratory Glassware

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REAGENTS

~~Benzene and~~ Toluene ethyl ether-nanograde or equivalent

Sodium sulfate - anhydrous, reagent grade

Florisil - 60/100 mesh Floridin Corp.

10% ethyl ether-benzene solution

Linuron Standard - E. I. duPont Analytical Standard

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PROCEDURES

A. Preparation

The frozen sample is chopped thoroughly in a Hobart Salad Maker.

B. Extraction

A 100 gm portion of the chopped asparagus together with 50 gms of anhydrous sodium sulfate is placed in cup of the omnimixer, 400 ml of nanograde benzene is added and the mixture is blended at high speed for five minutes. At the end of this time the mixture is filtered through anhydrous sodium sulfate into a 100 ml volumetric flask (equivalent to 25 gms of original sample). The filtrate is concentrated to approximately 5 ml by distillation in vacuo in a hot water bath.

C. Column Chromatography

A plug of Pyrex glass wool is placed in the chromatographic tube as a support. The column is packed to a height of 4 inches with Florisil which is in turn topped with 1 inch of anhydrous sodium sulfate. The packing is prewashed with 50 ml of nanograde benzene withdrawing the wash liquid until the top surface just enters the sodium sulfate layer. The 5 ml of extract from "B" is added to the column and the sample container rinsed with two successive 5 ml-portions of nanograde benzene which are added in turn to the top of the column. When the solvent surface again enters the sodium sulfate layer, 200 ml of 10% ethyl ether in benzene is added, the receiver changed and the eluate retained until the surface of the elution solvent reaches the sodium sulfate. The eluate is concentrated to a volume of 2 to 3 ml, transferred quantitatively with benzene washes to an appropriate screw-capped

Part 5
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vial and taken to dryness with a nitrogen sweep in a hot water bath. The residue is dissolved in 0.5 ml of nanograde benzene.

D. Gas Chromatographic Analysis

The benzene solution from "C" is analyzed by gas-liquid chromatography using the following conditions:

Column temperature	200° C
Injection port temperature	220° C
Helium carrier gas flow	15 ml/min
Bridge setting	30 volts
Attenuation	1
Aliquot	10 microliters
Quantitation	peak height
Retention time	2.5 minutes

E. Calibration

Several 10 ul aliquots of a reference solution of linuron containing the quantity of pesticide estimated to be present in the sample are analyzed along with 10 ul aliquots of the asparagus extracts.

F. Calculations

The general formula for calculation is as follows:

$$\text{ppm} = \frac{\text{micrograms found}}{\text{sample wt. in gms.}} = \frac{\text{nanograms in aliquot injected}}{\text{mg sample in aliquot injected}}$$

If a standard curve of nanograms vs peak height is used, the quantity in the aliquot is read directly from the curve. The sample weight in the aliquot is then calculated by the following method:

Twenty-five grams of the crop taken through the cleanup and diluted to 0.5 mls will yield 50 gms/ml or 50 mg/ul. A 10 ul injection will then contain 500 mg. of sample.

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An alternate calculation without standard curve is as follows:

$$\text{ppm} = \frac{\text{conc. in standard solu (mg/ml)}}{\text{sample weight through cleanup/gms}} \times \frac{\text{peak height sample}}{\text{peak height standard}}$$

X final vol of sample soln. (ml)

G. Recovery Studies and Sensitivity

Typical chromatograms are shown in Figures I through III. Figure I is a standard curve of concentration vs. peak height developed on the Varian Aerograph 2100. Figures II and III are recovery studies made with asparagus samples fortified with 0.2 ppms of linuron. Figure III also includes analytical curves from a study made at El Centro in 1971. The results derived from these studies are included in tabular form in the original data package submitted to E.P.A.

Results from recovery studies at both 0.2 ppm and 0.5 ppm are shown below:

	0.2 ppm	0.5 ppm
	96 %	100 %
	100 %	100 %
	74 %	82 %
	77 %	
Σ	347	282
$\bar{X}$	86.7%	94%
range		

The sensitivity with the aliquot size used in these studies is 0.1 ppm for a 5 cm deflection with an estimated detection limit of 0.05 ppm. Larger aliquots would increase the sensitivity.

(6)

LINURON RECOVERIES FROM

ASPARAGUS BY ALKALINE HYDROLYSIS
(200 gram samples)

Fortification ppm	µL Injected	Gms Sample Injected	mm Response	Nanograms Response	ppm Recovered	Percent Recovered
1.0	8	0.314	158	322	1.03	103
0.25	15	1.23	125*	250	0.203	81

* Average of two

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D93622-B

3,4-DICHLOROALINE STANDARD

(160°C MICROCOULOMETRIC DETECTOR)

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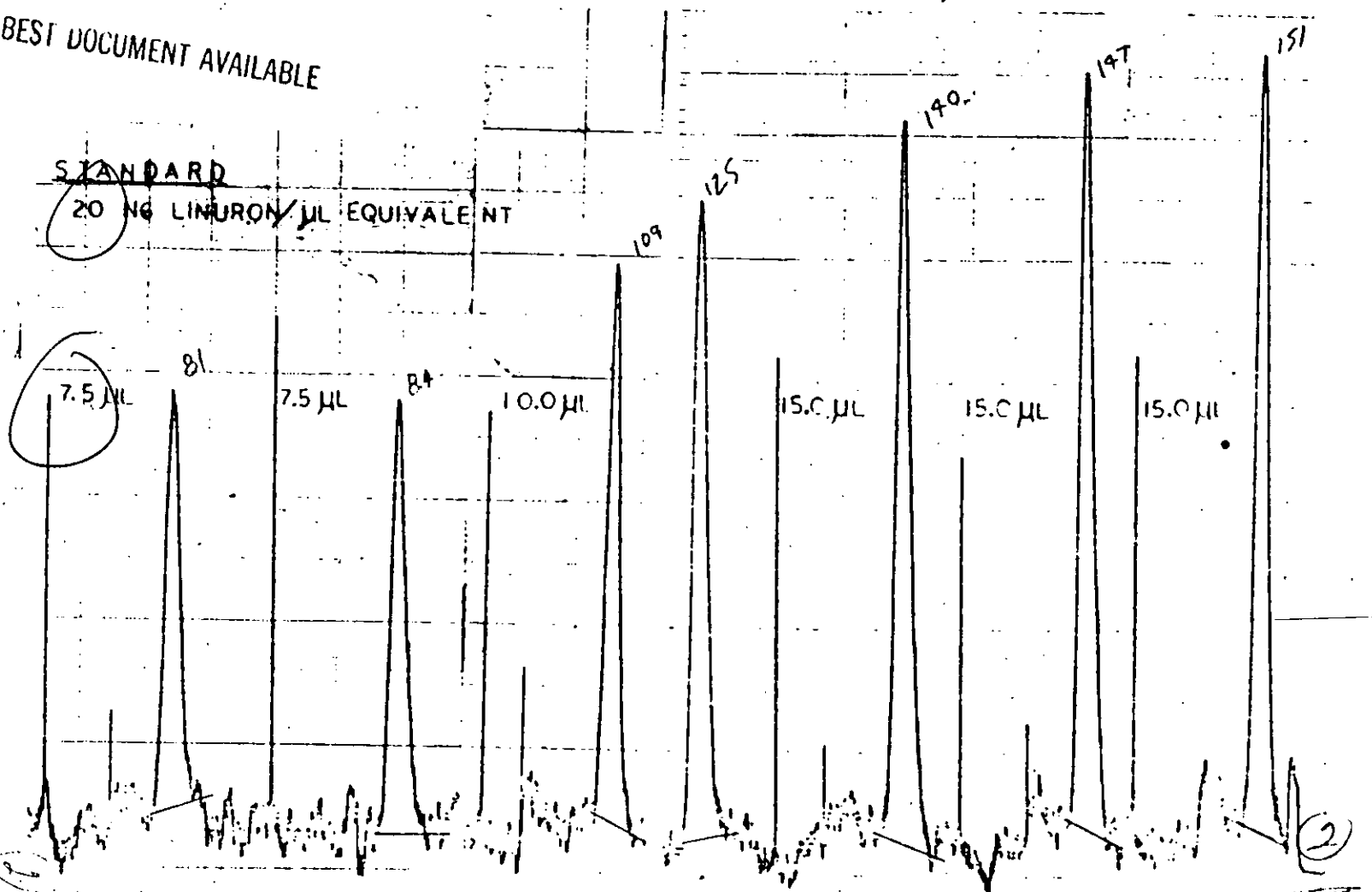
STANDARD

20 NG LINURON/µL EQUIVALENT



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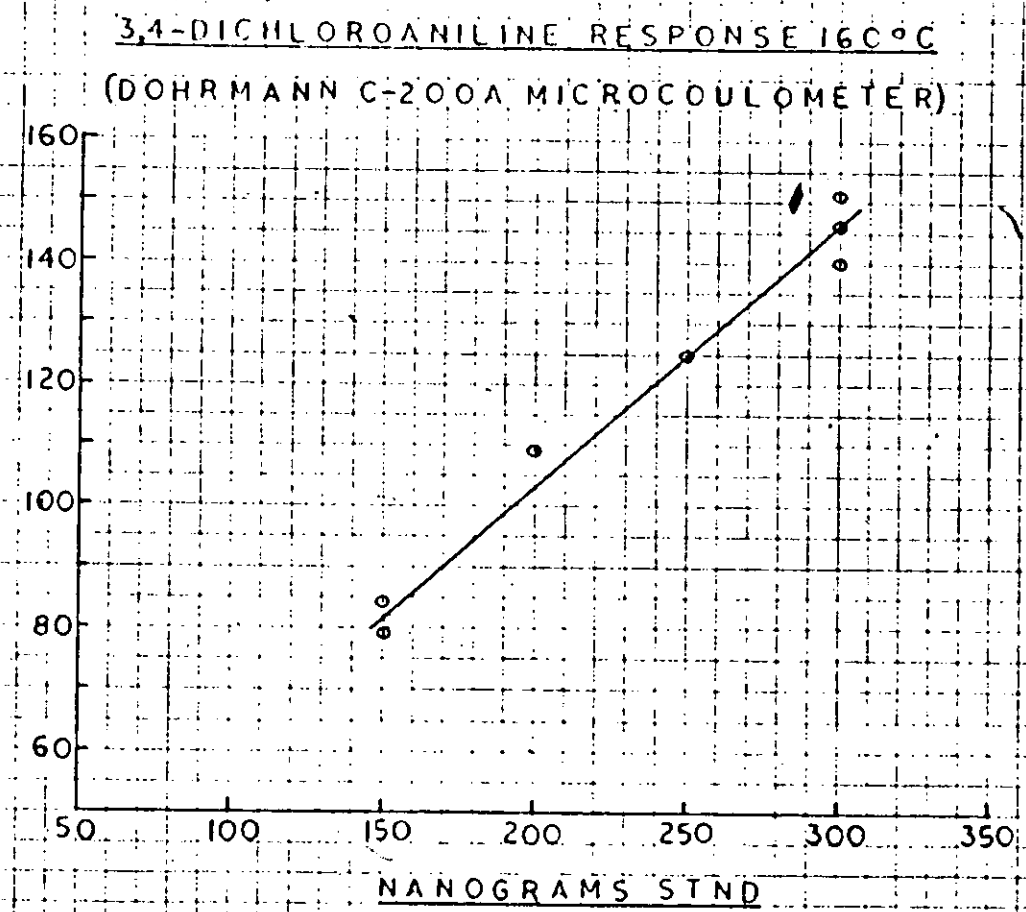

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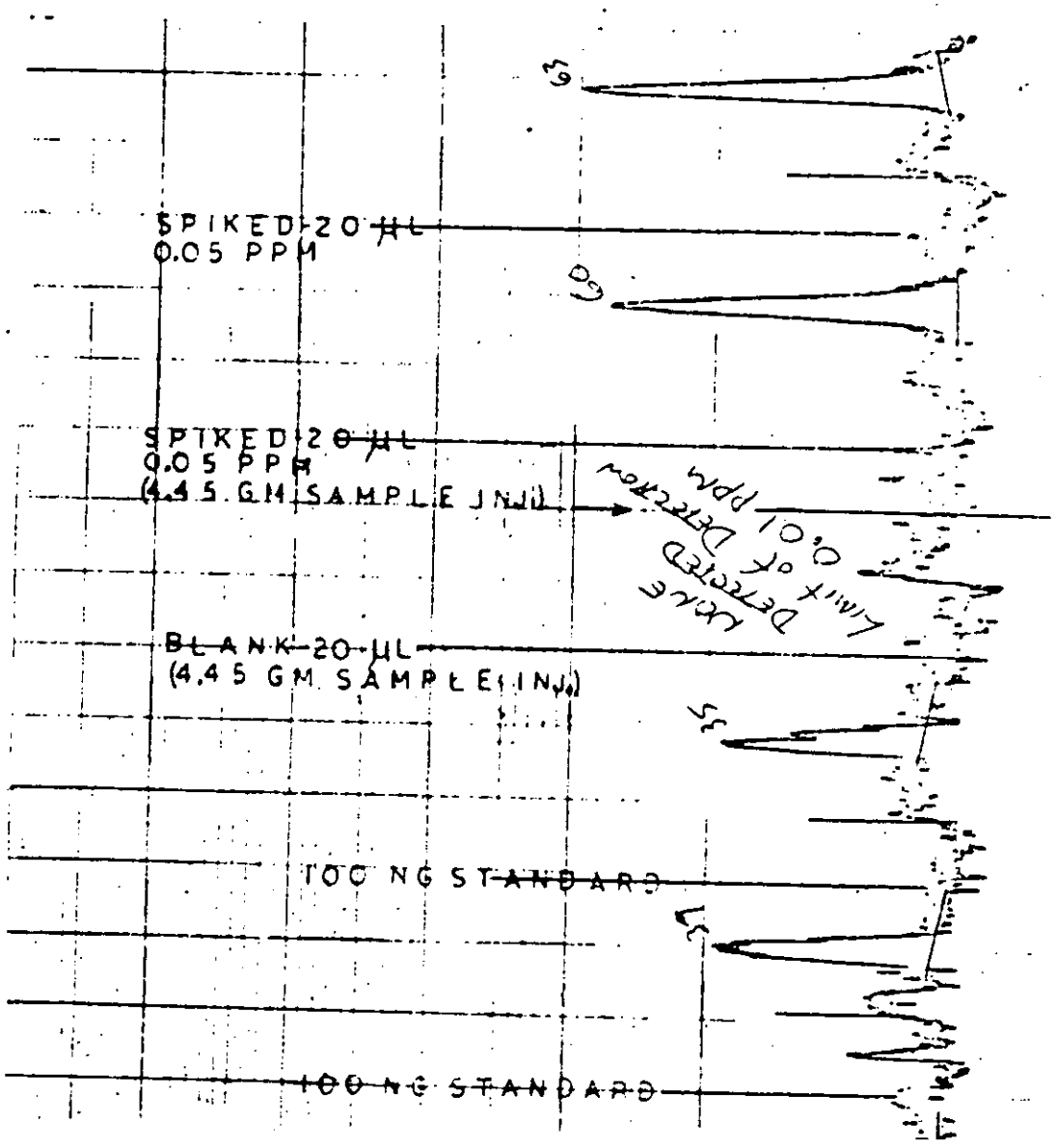
ASPARAGUS BLANK
(160°C MICROCOULOMETRIC DETECTOR)



LINURON RECOVERY STUDIES 7-31-74

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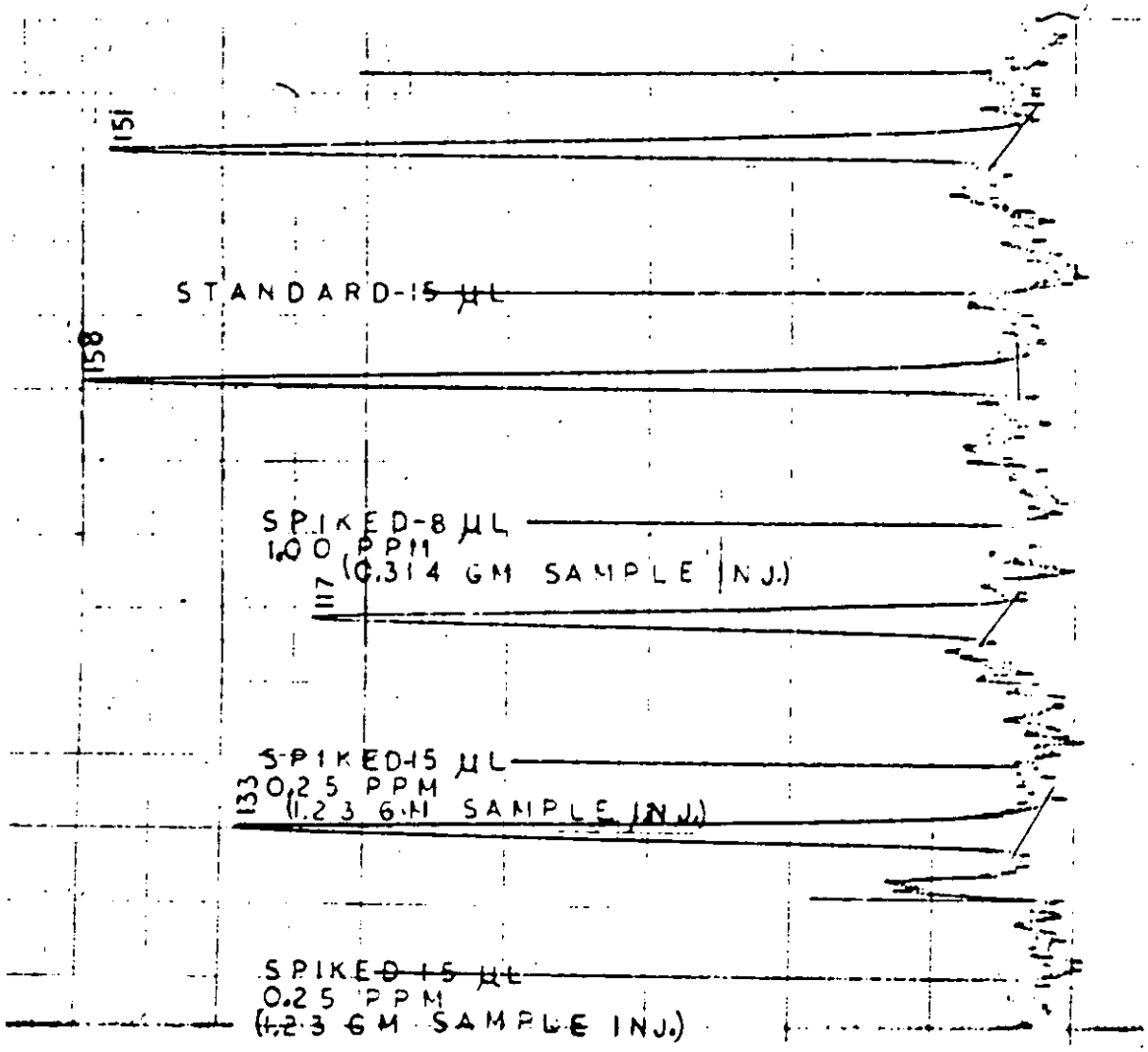
SPIKED ASPARAGUS
(160°C MICROCOULOMETRIC DETECTOR)



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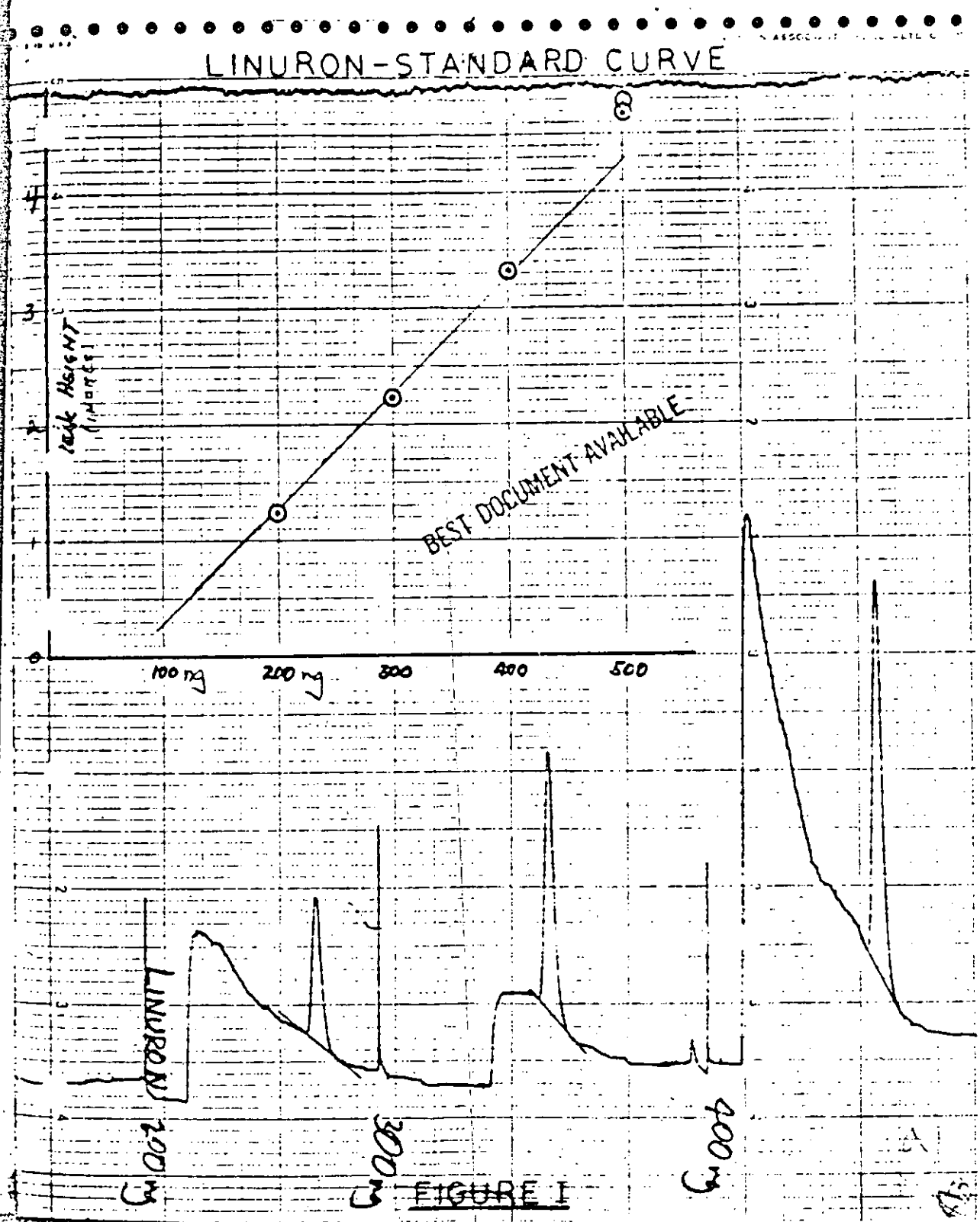

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FIGURE I

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LINURON-RECOVERY FROM ASPARAGUS

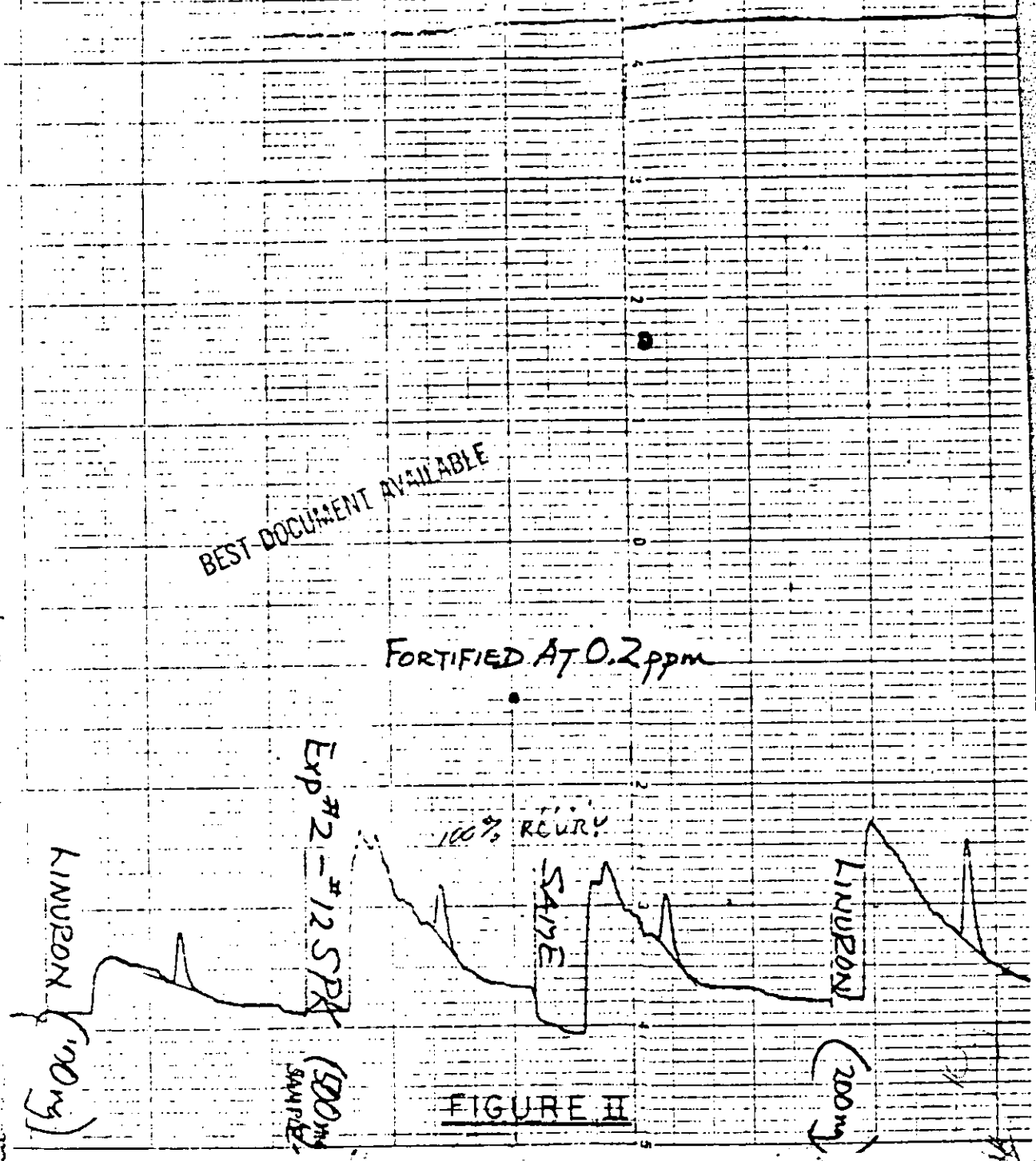

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FIGURE II

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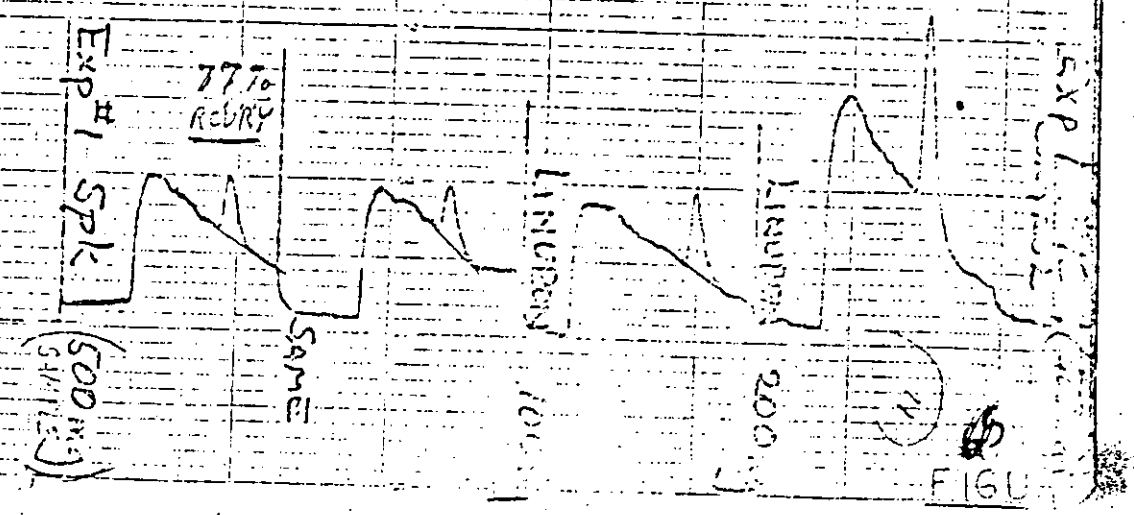
LINURON RESIDUES - EL CENTRO, CALIF.

36991 - 9992

APPLIED 1-8-71

RATE LB/A	LAB. NO.	EXP. NO.
1.5 LB.	36991	1-3
3.0 LB	36992	1-6
6.0 LB	36993	1-9
CONTROL	36994	1-12
SPIKE 0.2 PPM		1

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